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HARDWARE, SOFTWARE, AND OPERATIONAL PROCEDURES FOR AN EXTRACTIVE FT-IR AIR MONITORING SYSTEM

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The report provides a general background for extractive sampling with FT-IR spectroscopy. The report also documents the procedures necessary to validate the performance of an FT-IR spectrometer used in an extractive sampling application. The design, fabrication, and implementation of an extractive FT-IR system are demonstrated. Alignment methods for a 10-m optical gas cell and FT-IR spectrometer is furnished in a step-by-step procedure list. Creation of reference spectra is shown for a target analyte of ethanol at 200 °C. Appendixes contain details on (1) FT-IR spectrometer hardware, (2) sampling protocols for extractive FT-IR spectroscopy, and (3) baseline spectra of ethanol and ethylene simulants.

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PREFACE

The work described in this report was authorized under Contract No. DAAD05-97-P-3045. This work was started in August 1997 and completed in December 1997.

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CONTENTS

HARDWARE, SOFTWARE, AND OPERATIONAL PROCEDURES FOR AN EXTRACTIVE FT-IR AIR MONITORING SYSTEM

I. Introduction

This manual has been written specifically to accompany the FT-IR system constructed by AeroSurvey, Inc. and delivered to the U.S. Army ERDEC in November 1997, under contract DAAD-97-P-3045. As the system was intended for applications in the demilitarization effort, the instrument is referred to as the ASI/Demil FT-IR system in this document.

The purpose of this manual is twofold. The first objective of this document is to provide a general introductory background in FT-IR and particularly extractive FT-IR sampling. This general background discussion is non-rigorous and, for readers who are experienced with FT-IR, this may not need to be reviewed. For readers who are not familiar with FT-IR techniques, it is hoped that this section will provide a basis for understanding the operation of the ASI/Demil FT-IR system that would be unavailable from the step-by-step procedures alone.

The second and main objective of this documentation is to document performance validation data collected by AeroSurvey immediately prior to delivery of the system. It is hoped that this documentation will serve as a reference point for trouble-shooting the spectrometer hardware, software, and the associated analytical procedures..

The procedures detailed in this manual are not application specific. Rather, the procedures are generally applicable to the use of the modified spectrometer system for sampling ambient temperature gases.

The format of this manual is to present the general background materials first, followed by discussions of the system's hardware components and software operational procedures, and, finally, a step by step procedure for the collection of laboratory calibration and field sample data.

There are also four appendices in this manual. The first appendix is a detailed list of the hardware and software delivered by AeroSurvey, Inc. with the ASI/Demil FT-IR system.

The second appendix is a sampling protocol for the general application of extractive FT-IR for gaseous sampling (1). This protocol is approved by the U.S. EPA and is generally accepted as the most rigorous sampling protocol available for extractive FT-IR monitoring.

The third appendix documents the collection of baseline system performance and calibration data. Validation data, collected with the step-by-step procedure outlined in the body of this manual, is presented for ethylene and ethanol.

Data relating to the gas flow and purging characteristics of the ASI/Demil FT-IR system as delivered is presented in Appendix 4. This data provides a basis for establishing flow rates, purge times and data collection times in application-specific protocols to be developed in the future.

I.A. Spectroscopic background: Basic FT-IR theory, operation, and design

In this introductory section, the principles of infrared spectroscopy and FT-IR spectrometer operation will be presented in a non-rigorous manner for the benefit of those readers with a limited background in infrared analytical techniques. Readers with an understanding of these subjects may safely forego this discussion and proceed to subsequent sections. Conversely, readers desiring a more rigorous and thorough discussion of the concepts presented in this introductory section are referred to the relevant texts listed as references at the end of this introductory section.(1,2,3)

I.A.1 The origins of infrared absorption bands

Spectroscopy is the study of interactions between matter and energy. *Infrared* spectroscopy is often referred to as *vibrational* spectroscopy or *molecular* spectroscopy because the absorption and emission of infrared light energy by a sample is due to vibrational energy transitions by the molecules comprising the sample under study. The bonds between the atoms of a molecule are flexible and are often compared to springs connecting two masses. The analogy is in many ways a good one and the vibrational behavior of molecular bonds can be largely explained in the same terms used to describe the behavior of ideal springs in a first-semester physics course.

Like a spring, a molecular bond exerts a restoring force on the motion of masses attached to it; the atoms attached via the bond display a periodicity in their motion. The flexibility of molecular bonds allows the atoms of a molecule to move relative to one another with either an in-and-out stretching motion or a side-to-side bending motion, similar to masses on a real spring. The possible vibrational motions for a given molecule are referred to as the vibrational modes of the molecule. Each vibrational mode may potentially give rise to an infrared absorption band, as will be illustrated shortly.

As an example of vibrational modes, consider the relatively simple molecular structure of carbon dioxide, CO_2. Each of the two oxygen atoms are bonded to the central carbon atom and the molecule is linear. The covalent bonds between the atoms are flexible, though, and three vibrational modes are possible for CO_2. One of the vibrational modes possible for CO_2 is a bending mode, in which the oxygen atoms wag back and forth along short arcs around the central carbon atom. There are also two vibrational stretching modes possible for CO_2: a symmetric stretch in which the two C = O bonds lengthen and shorten in unison and an asymmetric stretch in which one bond lengthens while the other shortens. These three modes are labeled ν_1, ν_2, and ν_3, according to the diagram shown in Figure I.A.1.

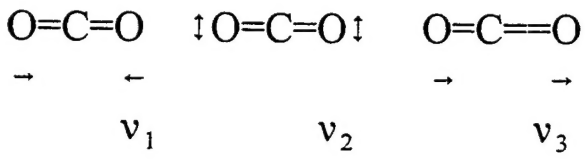

Figure I.A.1. The vibrational modes of CO_2. The ν_2 mode is responsible for carbon dioxide's fundamental infrared absorption band at 667 cm-1, the ν_3 mode is responsible for carbon dioxide's fundamental infrared absorption band at 2350 cm-1, and the ν_1 mode is infrared inactive because vibrations in this mode do not induce any change in the molecule's dipole moment.

Unlike a system of masses attached to ideal springs, however, the various vibrational modes of a molecule will have only certain discreet energy states in which they may vibrate, due to the quantum nature of matter at the molecular level. Also, the lowest energy state for each vibrational mode of a molecule (called it's ground state) is non-zero in magnitude. A molecule can change vibrational energy states in one or more of it's vibrational modes by the absorption or emission of the amount of energy that is the exact *difference* between two energy states.

One way that energy can enter and leave molecules, and thus cause transitions in vibrational energy states, is via photon interaction. A photon of light can be described by the amount of energy it represents. In the visible region of the electromagnetic spectrum, the different colors of light dispersed by a prism correspond to photons of different energies. The energies of photons in the infrared portion of the spectrum correspond to the energy differences that exist between vibrational energy states in molecules. *Photons of infrared light that strike a molecule can be absorbed if the photo n energy exactly matches the energy required to "kick" the molecule from one vibrational energy state to a higher state. It is these photon/molecule interactions that result in the infrared absorption bands that characterize almost every molecule.*

Returning to our CO_2 example, the infrared spectrum of CO_2 shows two distinct bands, one centered at 667 cm^{-1} and another at 2350 cm^{-1}. (Called *wavenumbers*, cm^{-1} are the units used by infrared spectroscopists to describe light at different frequencies. Wavenumbers are directly proportional to energy and inversely related to wavelength. A photon of infrared light at 667 cm^{-1} corresponds to light with a wavelength of approximately 15 micrometers.) Figure I.A.2 shows a percent transmittance spectrum of CO_2 in which these bands can be seen. The band at 667 cm^{-1} is due to the ν_2 vibration making a transition from its ground state to its first excited energy

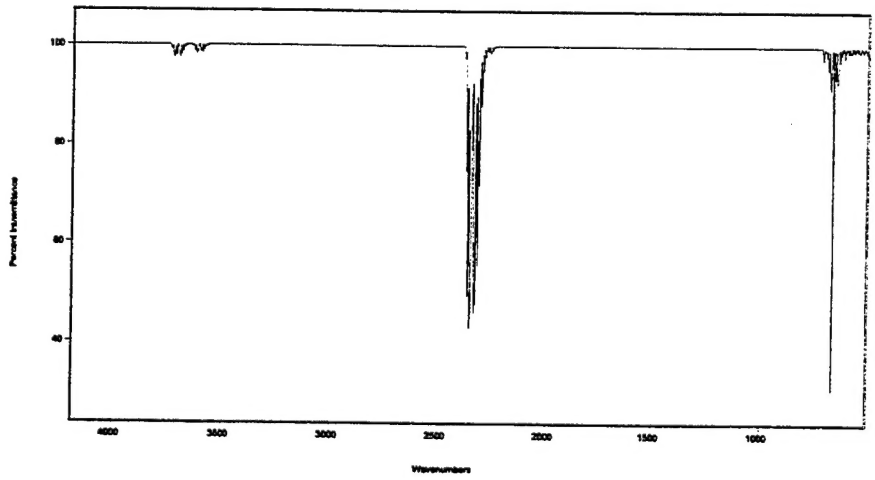

Figure I.A.2. A percent transmittance spectrum of carbon dioxide, displaying the fundamental absorption bands at 667 cm^{-1} and 2350 cm^{-1} and combinations bands at 3613 cm^{-1} and 3715 cm^{-1}.

state. Additional side-bands around the band center at 667 cm^{-1} are due to coupling of lower-energy rotational transitions to the 667 cm^{-1} vibrational transition. Similarly, the 2350 cm^{-1} band is due to photon absorption that results in the ν_3 vibrational mode jumping from its ground state to its first excited state. These bands are termed *fundamental* bands because they involve transitions from the ground state to the first excited state in their respective vibrational modes. All of the bands displayed by CO_2 provide a spectroscopic fingerprint for carbon dioxide *The power of infrared spectroscopy as an analytical tool comes from the fact that most molecules display a unique infrared fingerprint because of differences in the bonds and atoms that comprise the molecular structure of the compound.*

There is no fundamental infrared absorption band for the ν_1 vibrational mode of CO_2 - in the terminology of spectroscopists, the vibrational mode is not *infrared active.* This is because the ν_1 vibrational mode does not change the dipole moment in the CO_2 molecule - i.e., the electron charge density remains centered around the middle of the molecule during the ν_1 symmetric stretch. In general, only vibrational modes that induce an oscillating dipole can result in direct photon absorption. This same condition is responsible for the lack of any infrared absorption bands by molecules such as O_2, N_2, and Cl_2. Homonuclear diatomic molecules such as these are the only type of molecules that are not *infrared active-* i.e., do not display any infrared absorption bands. The only vibrational mode possible for such molecules is a symmetric stretch and, with both atoms of equal electronegativity, such stretches do not result in a change in dipole moment.

So, except for homonuclear diatomics, most molecules display characteristic infrared absorption bands. Most molecules display multiple bands. The intensity of the various bands varies between different molecules and even between the different bands of the same molecule. Therefore, qualitative spectroscopic analysis requires knowledge of each analyte's band locations and quantitative analysis requires knowledge of each band's intensity as a function of the amount of analyte present in the infrared sampling beam.

The appearance and spectral location of a compound's infrared absorption bands are a function of the compound's structure. Although two compounds may have bands that appear at approximately the same location in the infrared spectrum, it is still likely that the two compounds can be differentiated from one another because of different band shapes. Some bands are very broad and featureless while other bands, especially those associated with small molecules, display multiple branches and even discreet lines when recorded using spectral resolution capable of resolving them.

Figure I.A.3 shows reference spectra for benzene, toluene and meta-xylene, displaying some of each compound's fundamental bands. Also shown in Figure I.A.3 is a composite spectrum, displaying the bands of all three of these potential analytes. Note the individual appearance of each analyte's bands, in terms of location, relative intensity, and shape. Although these bands overlap in the composite spectrum, the spectral resolution allows the bands to be distinguished from one another.

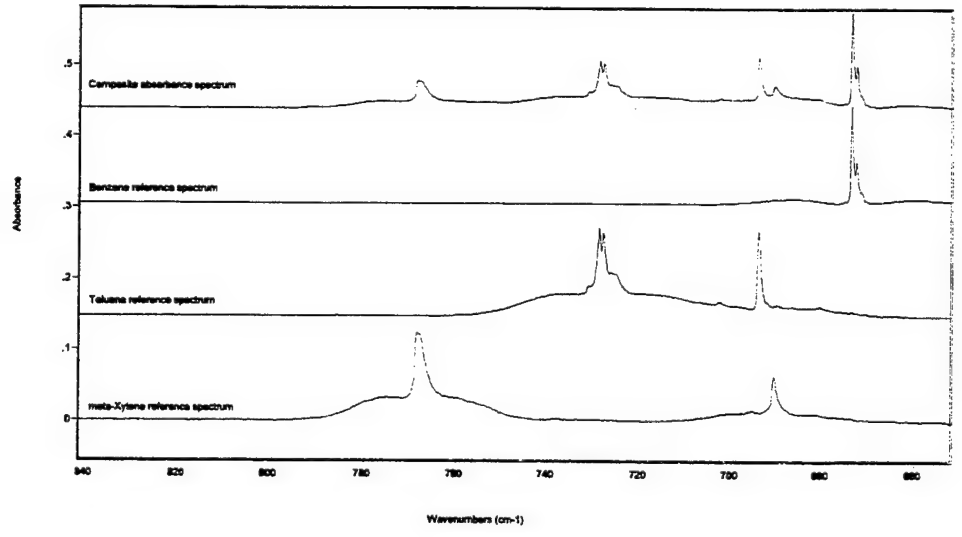

Figure I.A.3. A composite spectrum of benzene, toluene, meta-xylene and each separate reference spectrum.

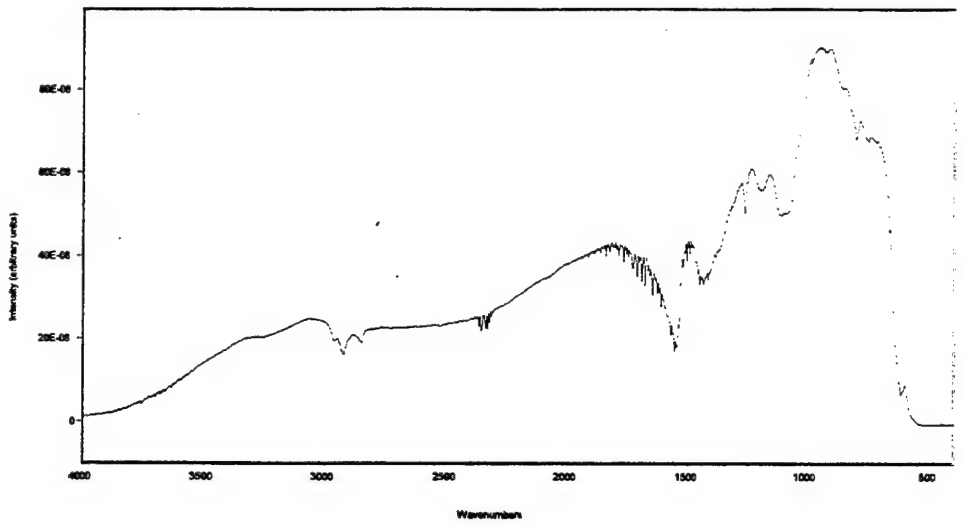

Figure I.A.4. A single-beam sample spectrum of carbon dioxide.

Often, analytes appearing in the same spectra with overlapping bands will also display non-overlapping bands in other regions of the spectrum that can be used as confirmatory bands to further reduce uncertainty in band identification. In addition to weaker fundamental bands, molecules may also display *overtone* bands at higher frequencies (typically in the near-infrared portion of the spectrum) that are the result of transitions to higher excited states and *combination* bands that result from coordinated energy transitions in more than a single vibrational mode. In general, overtone and combination bands are much weaker than fundamental bands. It is fundamental bands upon which most quantitative FT-IR measurements are based

I.A.2 Recording infrared absorbance spectra

In the example involving CO_2 presented earlier, the energy of the 667 cm^{-1} photon was converted to vibrational energy in the molecule and the photon disappeared in the process. On a macroscopic scale, this phenomenon results in the absorption of 667 cm^{-1} light by any sample containing carbon dioxide molecules. If one analyzes broadband infrared light that has been passed through a gas cell containing carbon dioxide, 667 cm^{-1} light will have decreased intensity and the carbon dioxide is thus detected. The amount of 667 cm^{-1} light that is absorbed depends on the number of carbon dioxide molecules encountered by the infrared beam as it passes through the sample. Shown in Figures I.A.4, I.A.5, and I.A.6 are spectra illustrating the effects of CO_2 absorption, displayed in a number of formats to be explained shortly.

Figure I.A.4 is a *single-beam* spectrum and it represents the signal produced by passing the infrared beam through a single sample space. The appearance of a single-beam spectrum is the cumulative result of many factors including the energy radiating from the infrared source, any absorptions by intervening analytes, interferents, or optical components, and the detector's frequency-dependent response function. In Figure I.A.4, the broad dips and peaks are largely due to the detector's response characteristics. The fine lines between approximately 1300 cm^{-1} and 2000 cm^{-1} are due to absorption by atmospheric water that was in the spectrometer's beam path - an interferant, in this case. Absorptions by the ν_3 band of CO_2 around 2350 cm^{-1} and the ν_2 band of CO_2 at 667 cm^{-1} appear relatively insignificant in this spectrum. The carbon dioxide responsible for the bands was in a gas cell placed in the infrared beam path of the spectrometer. More carbon dioxide in the beam path would have resulted in more intense absorptions by these bands. The relationship between the amount of an infrared absorbing compound and the intensity of the absorption bands in single-beam spectra is not linear, however.

Figures I.A.5 and I.A.6 are termed *dual-beam* (or, often, *double-beam*) spectra, because they have been created from two beams passing through separate spaces, a sample space and a background space. (In this case, the background space and sample space differed more in time and condition than spatiality. The background single-beam spectrum was collected first, carbon dioxide was introduced into the cell, and then the sample single-beam spectrum was collected.) *Background single- beam spectra* are spectra of the sample space without any analyte. *Sample single-beam spectra* are spectra of the sample space when analyte is present.

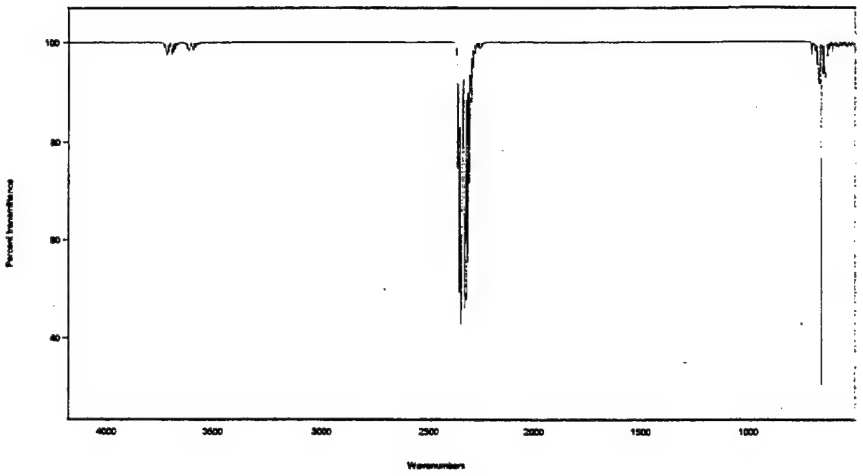

Figure I.A.5. A percent transmittance spectrum of carbon dioxide.

As was just seen in the Figure I.A.4 single-beam, many factors such as detector response affect the appearance of single-beam spectra. The main advantage of dual-beam spectra is that most of these instrumental factors cancel out in the mathematical operation (which involve either division or subtraction) used to create them. Only the factors that change in the two single-beam spectra being compared, such as the presence or absence of some analyte compound, appear in the dual-beam spectra. Removing the instrumental effects makes the spectral signatures of interest much more apparent, as evidenced in Figures I.A.5 and 6 by the appearance of relatively weak carbon dioxide overtone and combination

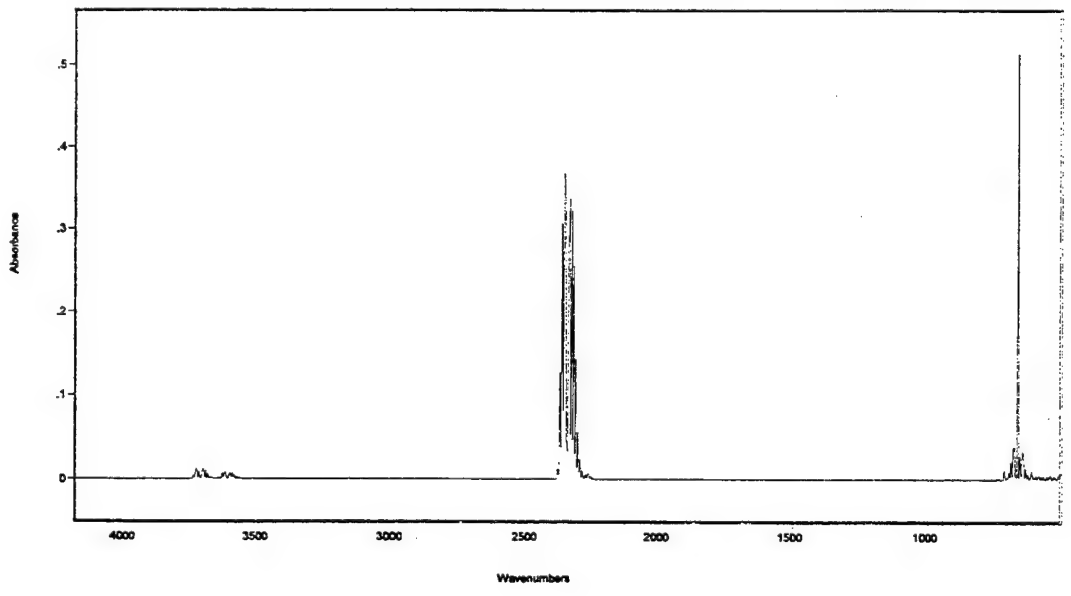

Figure I.A.6. An absorbance spectrum of carbon dioxide.

bands at 3613 cm^{-1} and 3715 cm^{-1}.

A *transmittance* spectrum is one type of a double-beam spectrum, where transmittance, τ, is the frequency-dependent ratio of a sample single-beam spectrum, I, to a background single-beam spectrum, I_0:

$$\tau_{\tilde{\nu}} = \frac{I}{I_0}$$

Figure I.A.5 is a *percent transmittance* spectrum, created by assigning the Figure I.A.4 single-beam spectrum as a sample single-beam spectrum, dividing it point-for-point by a background single-beam spectrum, and multiplying the result by 100 %.

As explained earlier, the background spectrum was nearly identical to the sample single-beam in Figure I.A.4 except for the absence of the carbon dioxide bands and it was collected over the same beam path as the sample spectrum. Percent transmittance spectra are simply interpreted as the percent of light (frequency-dependent) transmitted through a sample; molecular absorptions appear as regions of decreased transmittance. Although most of the factors affecting the detector's response have been eliminated in this type of dual-beam spectrum, there is still a non-linear relationship between the amount of carbon dioxide in the beam and the intensities of the analyte bands appearing in the spectrum.

Quantitative infrared analysis is most commonly based on *absorbance* spectra (note absorbance and not absorption), where absorbance is defined as the negative log of transmittance:

$$A_{\tilde{\nu}} = -\log_{10}(\tau_{\tilde{\nu}}) = -\log_{10}(\frac{I}{I_0})$$

Figure I.A.6 is an absorbance spectrum created from the sample single-beam spectrum shown in Figure I.A.4 and a background single-beam spectrum. The molecular absorptions that appeared as downward pointing bands of decreased transmission in the percent transmittance spectrum now appear as upward pointing bands, or absorbance bands, in the absorbance spectrum. By involving the logarithmic function in the generation of absorbance spectra, the intensities of analyte absorbance bands are linearly related to the amount of the analyte in the infrared beam

I.A.3 Infrared spectrometers and Fourier transform instruments

Commercially-available infrared spectrometers for the analysis of solid and liquid samples began appearing en masse in the 1950's and infrared spectroscopic analysis has been a mainstay of the laboratory chemist ever since. Special gas cells through which infrared light could be passed soon followed, allowing the infrared analysis of gaseous samples. A typical infrared spectrometer consists of a source of broadband infrared light, a sample space through which light from the source is passed, some mechanism for differentiating the various frequencies of light, and a photodetector.

With regard to the infrared source, the term *broadband* implies a continuous spectrum of all frequencies, in contrast to monochromatic light from a laser or light containing only certain discrete frequencies like that from a neon light. Heated objects, such as filaments in electric heaters, make good broadband sources of infrared light.

Early spectrometers were *dispersive* instruments, so called because they functioned by dispersing light into it's frequency components with a prism or a grating that functioned as a prism. After spatially separating the various frequency components of the light, a dispersive spectrometer measures the intensity of a single narrow frequency region at a time. A broad spectral region is investigated by scanning the dispersed frequencies over the detector. This approach to recording spectra typically results in somewhat fragile instruments, which have traditionally been restricted to the safe confines of a laboratory.

Certain technological advances in the 1960's made a new type of spectrometer possible, known as a Fourier transform (FT) spectrometer, and these instruments were soon widely available. Unlike dispersive spectrometers, FT spectrometers effectively measure the intensity of many frequencies of light at once, speeding the measurement process while providing higher quality data. This advantage, as well as many others, was immediately recognized in the new FT spectrometers and these advantages have helped to fuel a renewed interest in spectroscopic techniques during the last 25 years.

The heart of an FT spectrometer is an interferometer which splits the incoming light into two beams of equal intensity and then recombines them after causing the beams to travel different distances. When light beams are recombined after an optical path difference has been introduced in this manner, interference among the various frequencies of light causes some of the frequencies to be partially or wholly eliminated. The degree to which a particular frequency is attenuated by the interference depends on the path difference between the two beam halves.

Many different optical designs can be used to produce the interfering effect. The oldest design, called the Michelson interferometer, is still in use today and serves well to illustrate the operation of interferometers because of its simplicity. In a Michelson interferometer like that shown in Figure I.A.7, collimated light from the infrared source is split into two beams of equal intensity (half the light is transmitted

through the beamsplitter while the other half is reflected in a different direction). Both beam halves are reflected back to the beamsplitter. While one beam is reflected by a stationary mirror, a moving mirror reflects the other beam half. This introduces a range of optical path differences for the two beam halves, causing all frequencies to suffer varying degrees of destructive interference at various times in the moving mirror's scan.

The interference pattern (termed *interferogram*) created in the recombined beam halves by an interferometer is measured by a photodetector. Figure I.A.8 shows a portion of an interferogram including the *centerburst* which occurs at the point of *ZPD* (zero path difference). All frequencies of light are in phase at ZPD, no destructive interference occurs, and the light intensity on the detector is the greatest. As the moving mirror passes through ZPD and begins introducing greater optical path differences, fewer frequencies of light are in phase at any given point and the interferogram intensity quickly dampens out.

Interferometric data is often termed *time-domain* data because it represents the signal from the instrument as a function of time, as the moving mirror travels through a scan. A mathematical operation known as a *Fourier transform* converts time-domain data to *frequency- domain* data - i.e., a plot of intensity versus frequency. The single-beam spectrum shown in Figure I.A.4 is a result of applying the Fourier transform to the interferogram in Figure I.A.8.

As for the actual infrared detector, various types are available that operate on various principles but they all essentially respond to infrared light by altering their electrical characteristics in some way. These variations in voltage, current, or resistance are amplified electronically and sampled to create a digitized signal. Thermal detectors respond to the temperature changes incurred when they are subjected to infrared radiation. Quantum detectors respond to photons directly.

Quantum detectors offer a combination of response speed and sensitivity that cannot currently be matched by thermal detectors and are the most common type of detector in FT-IR systems designed for environmental applications. Quantum detectors based on a mercury-cadmium-telluride (MCT) material are favored in the mid-infrared region of the spectrum. Some systems designed for operation at higher infrared frequencies may use a quantum detector based on an indium antinomide (InSb) material.

Many infrared detectors, including MCT and InSb detectors, require cooling to operate and these detectors' analytical performance is inversely related to their operating temperature. Incorporating the detector into a dewar that holds liquid nitrogen is the simplest and most common approach to cooling these detectors. A supply of liquid nitrogen and periodic refilling of the detector dewar (typically every four to eight hours) is required for FT-IR systems that use liquid nitrogen for detector cooling.

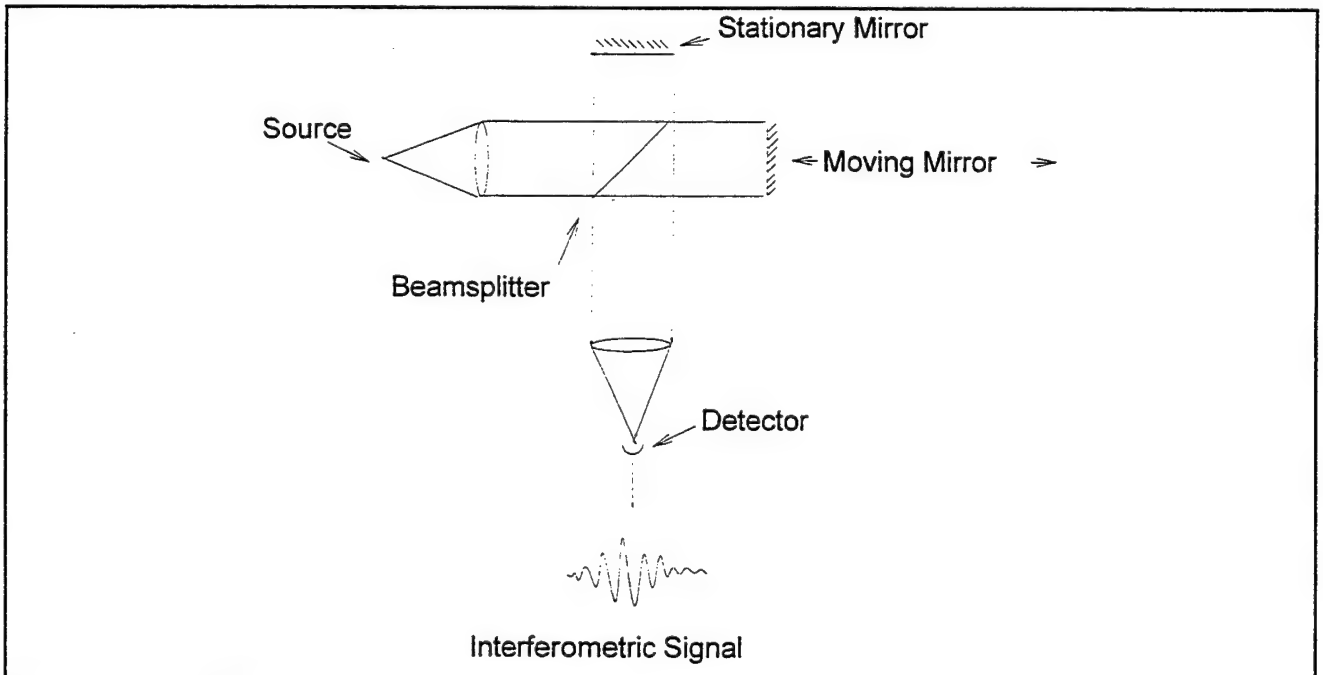

Figure I.A.7. A Michelson-type interferometer.

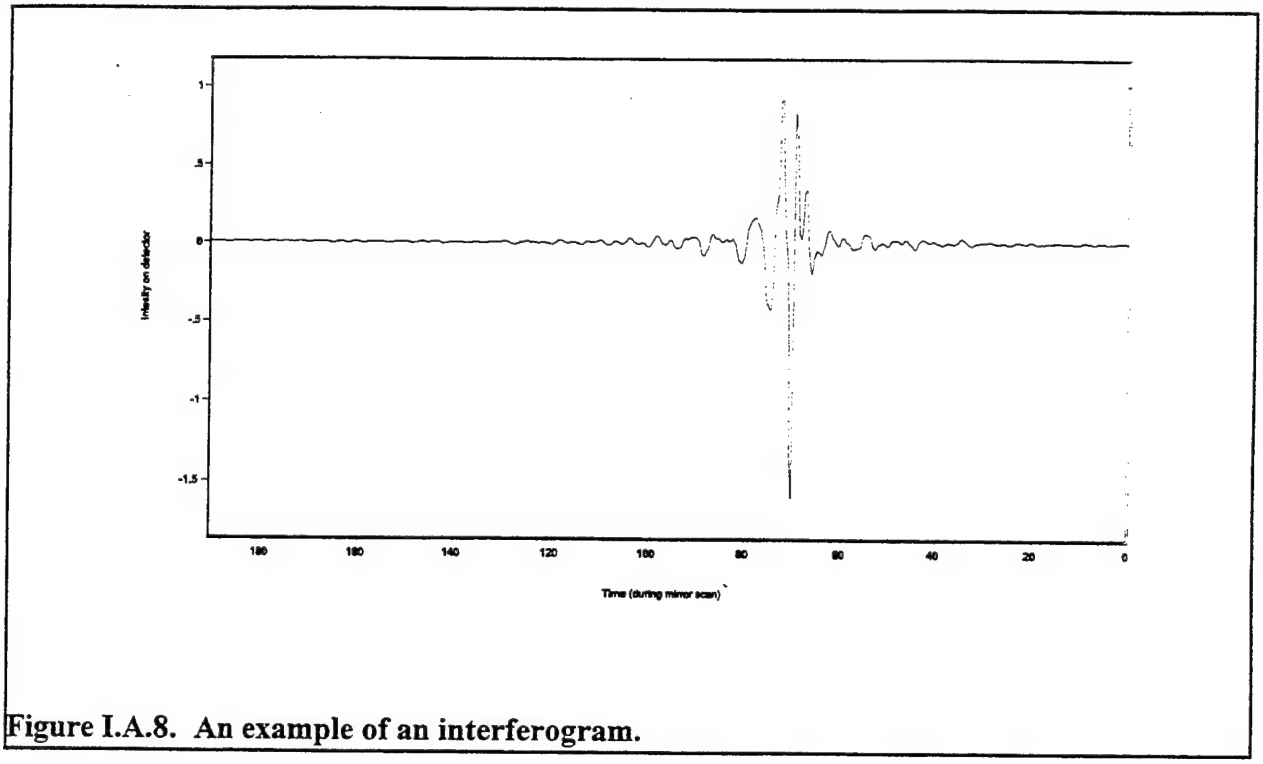

Figure I.A.8. An example of an interferogram.

Interest in applying FT-IR technology to field applications has driven the development of solid state and mechanical coolers. Solid state coolers (Peltier coolers) are not able to achieve the extremely low temperatures of liquid nitrogen and detector performance suffers accordingly, all else being equal. Nonetheless, Peltier cooling has proven itself to be a very reliable and convenient means of cooling infrared detectors, especially in FT-IR systems designed for long-term monitoring applications and in systems for which somewhat poorer detector performance can be tolerated or compensated. Examples of such applications would include those in which analyte concentrations are not so low as to require maximum sensitivity as well as almost all applications involving cell-based extractive sampling, when the use of multi-pass sampling cells can make even dilute samples appear optically dense.

Mechanical coolers are essentially miniature refrigeration units and have been incorporated into many FT-IR systems intended for field use, particularly open-path FT-IR monitoring systems. These coolers are convenient and can achieve liquid nitrogen temperatures. Unfortunately, mechanical coolers have traditionally been plagued by a number of drawbacks. Mechanical coolers can introduce vibration noise into the data that may offset the performance gains associated with their low operating temperatures. Mechanical coolers also have rather high purchase and maintenance costs. Manufacturers of mechanical coolers have been addressing these problems and improvements may be expected.

For environmental air monitoring applications, one of the most important advantages of FT-IR spectrometers has been that the FT-IR instrument itself has proven to be more rugged and amenable to field use than earlier dispersive instruments. Interest in using FT-IR spectrometers outside of the laboratory resulted in a flurry of research in the 1970's and 1980's.(5,6) Many open-path FT-IR systems for the field measurements of airborne analytes were developed in this period and FT-IR systems are now used regularly to analyze air samples for trace pollutants.

I.B. An introduction to infrared transmission characteristics of air

Figure I.B.1 is an infrared transmission spectrum of a typical air sample, created by passing a beam of broadband infrared light through approximately 4 meters of air. The MCT detector in the instrument used to collect this spectrum does not respond above 3500 cm-1 or below 600 cm-1. Between these two limits, infrared energy is seen to have largely passed through the air except for a few areas. The regions of decreased transmission are due to the atmospheric water and carbon dioxide in the path and are seen to be fairly significant, even over this relatively short path. Lesser

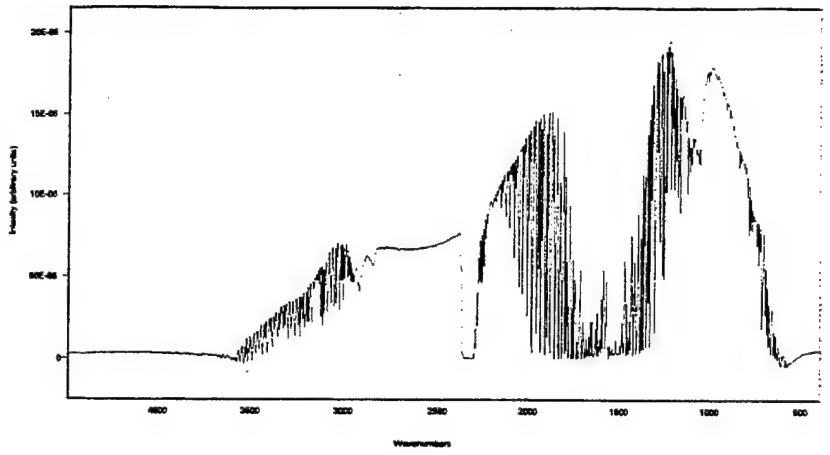

Figure I.B.1. A single-beam spectrum collected of an air sample, displaying the absorptions associated with air. This spectrum was collected with an open-path FT-IR system using an MCT detector over a pathlength of 4 meters.

absorptions are also present in the spectrum (though not necessarily observable in Figure I.B.1) due to other minor constituents of the air, including methane and carbon monoxide.

Between the regions of greatest absorption are regions of high transmission, often referred to as spectral "windows" of atmospheric transmission. Two regions in particular should be noted. The so-called "8 to 12 window" (8 μm to 12 μm) is framed by the low frequency edge of the strong ν_2 water band, around 1300 cm^{-1}, and a sharp and strong absorption band of carbon dioxide at 667 cm-1 (that coincides approximately with the detector cut-off for the instrument used to generate the spectrum in Figure I.B.1). The "3 to 5 window" (3 μm - 5 μm) exists between approximately 3000 cm^{-1} and 2450 cm^{-1}. The high frequency boundary for this window is a region of infrared absorptions due to multiple water bands while the low-frequency limit for this region is a sharp and strong carbon dioxide band centered at 2350 cm^{-1}.

Over the longer pathlengths common to open-path FT-IR air monitoring, atmospheric absorptions may become so intense as to make certain areas of the spectrum essentially opaque. Some regions will be opaque over even short pathlengths of a few meters or less, because the responsible absorption bands are very strong and there is a relatively large amount of water and carbon dioxide in air. Other regions will be attenuated by weaker bands but not completely opaque. The presence of minor water and carbon dioxide bands in a region does not necessarily eliminate the region from use completely. In fact, weak atmospheric bands appear almost everywhere in the infrared air spectrum, even in the so-called windows of atmospheric transmission. It is only when the energy absorptions by these bands become near-total that the region becomes unusable for infrared air monitoring purposes.

The bands due to atmospheric water and carbon dioxide are actually comprised of many sharp lines. In theory, high spectral resolution can allow one to use the some of the narrow regions that exist between the intense, sharp lines in the water and carbon dioxide bands. In practice, however, the use of narrow regions between strongly absorbing atmospheric bands is difficult at best, especially with the limited resolution capabilities of most commercially-available FT-IR instruments. Fortunately, most compounds display one or more absorption bands in less problematic spectral regions.

I.C. An introduction to extractive FT-IR: instrumentation, sampling systems, and instrument parameters

Extractive FT-IR systems are capable of providing both qualitative and quantitative information about the molecular constituents of a gas sample. As implied by the name of the technique, extractive FT-IR analysis involves pulling (extracting) a gas sample out of the original sample space and introducing the sample into an infrared gas cell for analysis by the spectrometer system. This procedure makes extractive FT-IR monitoring a point sampling technique.

The EPA has commissioned the development of an extractive FT-IR protocol, entitled "Protocol For The Use Of Extractive Fourier Transform Infrared (FT-IR) Spectrometry For The Analysis Of Gaseous Emissions From Stationary Sources".(1) This document is generally applicable to all

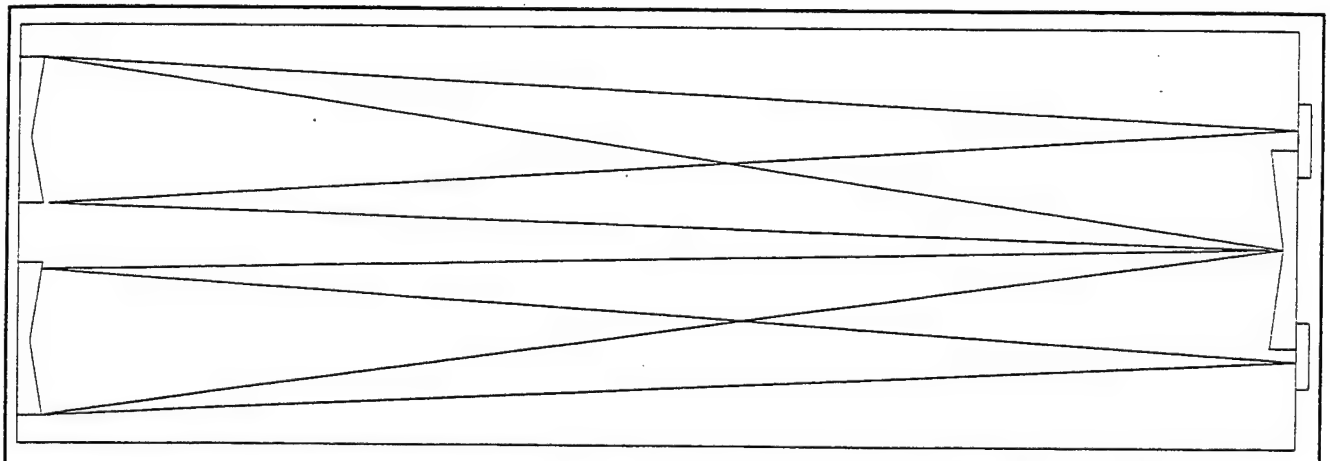

Figure I.C.1. The optical path through a multi-pass gas sampling cell (White cell), shown in a simplified fashion. Typically, cell mirrors will be aligned to produce many reflections back-and-forth through the cell before the beam is allowed to exit in order to produce longer effective pathlengths. (Diagram provided by of Infrared Analysis, Anaheim, Ca.)

extractive FT-IR applications and outlines very specific procedures for the collection and interpretation of extractive FT-IR data. Potential users of extractive FT-IR techniques, especially those operating in the realm of the EPA and similar regulatory agencies, are directed to this document for detailed information concerning the collection and interpretation of extractive FT-IR data.

This section will not attempt to duplicate or discuss the detailed information available in the EPA protocol document. Rather, the intent of this section will be to broadly introduce the instrumentation used to perform extractive FT-IR analysis, the sampling systems that are associated with extractive FT-IR analysis, and the data collection parameters used with extractive FT-IR methods for the benefit of readers with little or no previous familiarity with the technique.

I.C.1 Instrumentation in extractive FT-IR monitoring systems

Extractive FT-IR systems are generally based on the same Michelson type interferometers used in the laboratory. In most cases, the light generated by the infrared source is modulated by the interferometer, passed through the gas cell, and on to the detector. Variations among the commonly available systems primarily involve the design of the interferometer engine and configuration of the sample cell or cells. Assuming the interferometer design has been shown to function properly, only the cell configuration is of real concern to most users.

The most common configuration of the sampling cell used in extractive FT-IR systems is the White cell. The White cell is a type of multi-reflection gas cell. As Figure I.C.1 shows, the radiation that enters through the front window of a White cell is reflected between the end mirrors until the radiation escapes from the exit window. The effective pathlength achieved in a White cell depends on the dimensions of the cell and the number of reflections, but a cell with dimensions of approximately 0.3 meters in length and 0.1 meters in diameter can provide effective pathlengths as long as 10 meters.

Longer pathlengths afford lower detection limits, up to the point that SNR degradation due to beam attenuation while traversing the longer pathlength begins to overcome the effects of greater absorption signals. In well-designed cells, however, improvements in detection limits may continue to be realized even as effective pathlengths reach hundreds of meters in length.

White cells used in extractive FT-IR systems can either have adjustable or fixed pathlengths, and each type has its advantages and disadvantages. White cells with adjustable paths will have an adjustable mirror mount that allows the number of beam reflections to be changed, thus changing the cell's effective pathlength. An adjustable cell allows the user to change the dynamic range of the extractive FT-IR system to suit the given application; i.e., low concentration analytes can be monitored with a longer pathlength and high concentration analytes with a shorter pathlength. With an adjustable cell, however, both high and low concentrations of an analyte cannot be measured simultaneously. The dynamic range can be changed but not actually increased in an instrumental sense. Although alignment of this type of cell is not difficult, the fact that one

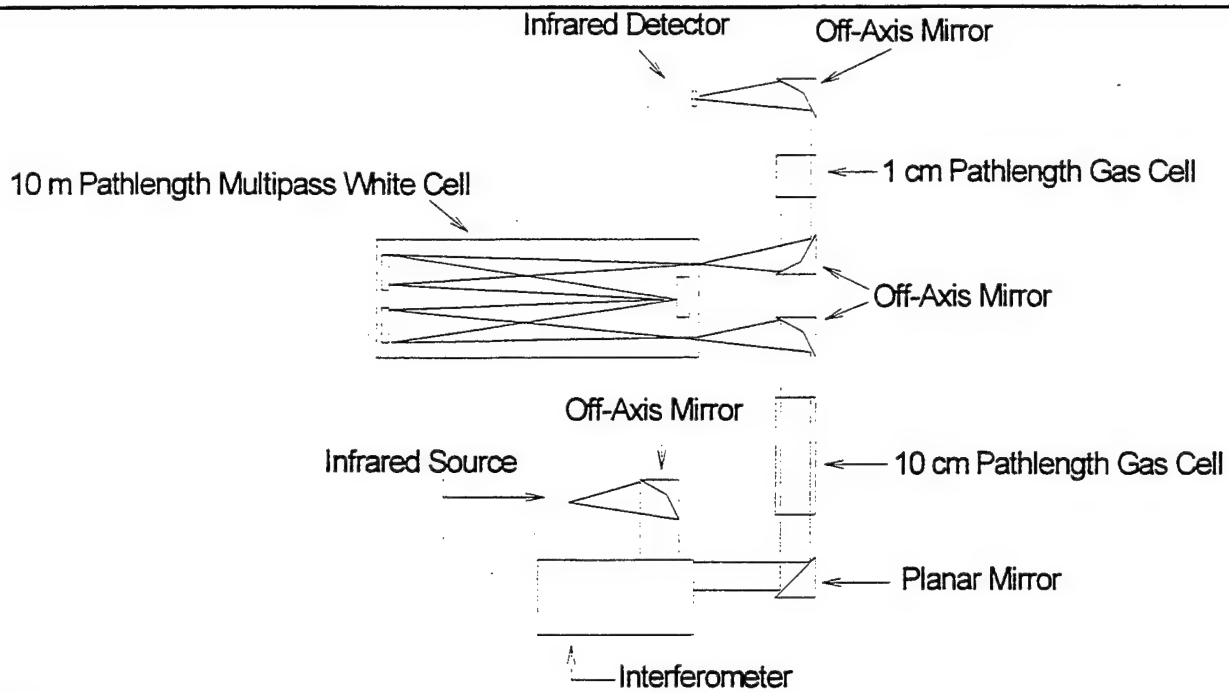

Figure I.C.2. A typical optical train for an extractive FT-IR monitoring system using multiple cells. (Diagram provided by Midac Corporation, Irvine, Ca.)

mirror in the cell is movable means that there is potential for the alignment to change slightly during use, especially in rugged environments. This type of system is excellent as a survey system that is required to monitor numerous different processes.

A White cell may also have a fixed pathlength. All mirrors are hard mounted to the body of a fixed path cell, resulting in permanent alignment at a set pathlength. Although this type of cell is not as flexible in application as the adjustable path cell, this cell is rugged and virtually guarantees sampling reproducability. Fixed path cells work well to monitor processes that do not change drastically over time.

An extractive FT-IR system may use more than a single cell. This type of system combines some of the advantages of fixed path and adjustable pathlength cells in a single instrument. Figure I.C.2 shows the optical train of such a system. Multiple cell systems combine some of the flexibility of adjustable pathlength cells with the ruggedness of the fixed path cells. These systems, however, are still not as flexible as a true adjustable pathlength system nor as rugged as a single fixed pathlength system. Multiple cell systems offer fewer pathlengths (typically two or three) than can be configured with systems incorporating an adjustable pathlength cell. The additional components of a multiple cell system often reduce the throughput and increase the alignment complexity relative to a single cell system with fixed pathlength. Multiple cell systems are, nonetheless, a good compromise for those applications that require monitoring of both high concentration analytes and low concentration analytes by the same system simultaneously.

Besides the number or type of gas cells, another consideration when choosing an extractive FT-IR system is portability. A variety of systems designs are commercially available, with some small enough to be mounted entirely on a small two-wheeled dolly while others require large bulky racks or optical benches; the system to be used depends upon the application. Smaller, highly portable systems may be used for survey work while the larger, more rugged systems may be preferable if the system is going to be dedicated to a particular process or mounted in an analyzer house.

Virtually all systems are capable of heating the gas cell. This capability is extremely important if the system will be used to analyze samples at elevated temperatures to prevent condensation of hot vapors in the gas cell. Although virtually all systems can heat the gas cell, systems with large sample cells may have a limited range of temperatures that can be achieved. The useful temperature range of the cell or cells in a given extractive FT-IR system should be determined before the system is used for any given application.

I.C.2 Sampling apparatus for extractive FT-IR systems

In many, if not most, analytical techniques involving extractive sampling, the actual sampling and sample conditioning can be as complicated a matter as the instrumental analysis of the extracted sample. This chapter will not attempt to describe all of the methods and techniques for extracting samples from various processes and environments for chemical analysis. Rather, the various concerns associated with extracting a sample for analysis via FT-IR techniques will be discussed along with general sampling approaches that address those concerns.

The different types of sampling apparatus that can be used with extractive FT-IR systems all perform the same task; i.e., delivery of the sample to the sample cell. One must remember that the spectrometer only analyzes what is in the cell and a suitable sampling location must be chosen in order to obtain a representative sample. Therefore, it is always best to determine any engineering considerations and study the chemistry involved in the process being monitored when determining at exactly what point the sample is to be extracted.

The sampling systems commonly used in extractive FT-IR monitoring can differ drastically in complexity. The most important aspect of the sampling system is temperature. When possible, the entire sampling system including the cell should be maintained at a temperature that is high enough to preclude any gasses that may be at elevated temperature in the sample from condensing. When it is not possible to match the temperature of the environment being monitored, sample conditioning systems must be employed to remove water that might otherwise condense at the cooler temperatures in the sampling systems. Sampling designs that allow for spiking trials are especially important in these instances so that potential analyte losses in the sample conditioning step can be characterized.

A particulate filter should usually be present somewhere in the line before the sample is introduced into the sample cell. For ambient air monitoring or applications where the samples are known to have few particulates, this component may not be so important. However, in general, the reduction of particulates introduced into the cell will reduce the wear and tear on the cell's optical components over the lifetime of the sample cell. The size of particulate filter required for any given application should be determined by the conditions and chemistry of the process being monitored.

There should also be a flow meter in the sampling system that allows one to determine the flow rate of gas through the sample cell. A flow meter allows the sample volume to be determined, and this capability is important for both purging the system and for back-calculating the total mass of analyte that is being monitored.

The simplest sampling system that may be used for extractive FT-IR monitoring is a small pump and some tubing. Some of the commercial systems currently available include an on-board pump and valve system directly linked to the sample cell and controlled by the operational software. This type of sampling system is convenient for collecting samples at ambient temperatures or performing quick surveys to determine where a leak may or may not be present.

Higher levels of sophistication in extractive FT-IR sampling may involve the use of a heated sample probe, heated sample lines and a heated sample pump. Heated sampling components allow the sampling of gases at elevated temperatures from stacks or other hot processes. Although this sampling system is straightforward, one must be careful to insulate all of the joints in the sample system so that no cold spots exist in the system where the sample may condense. This system works well for short term test projects, but does not provide the analyst with a means of efficiently generating quality assurance/ quality control (QA/QC) data.

The most sophisticated, and certainly the most analytically rigorous, type of sampling apparatus that may be used with extractive FT-IR systems involves a heated manifold like that shown in Figure I.C.3. Essentially, this system uses the same components as the sampling system just discussed, but allows more flexibility and more QA/QC type data to be obtained.

The flexibility that is afforded a user by the heated manifold system results from the fact that multiple sample lines can be run from the manifold. This allows the user to employ this sampling system with multiple instruments (FT-IR or other) simultaneously. Simultaneously sampling the same sample space obviously makes for excellent comparison data between different instrumentation and between different analytical techniques.

Although the flexibility provided by the heated manifold system is advantageous, the most important advantage of this type of sampling system is that it provides a means for introducing an analyte spike. An analyte spike is a known compound at a known concentration that can be sent through the sampling system at a known flow rate. Use of analyte spikes allow the dilution factor of the sampling system to be determined and can also help to detect leaks or sample loss due to sample conditioning or condensation within the sampling system.

I.C.3 Data collection in extractive FT-IR monitoring

The choice of the data collection parameters for an extractive FT-IR system is often straightforward. Extractive FT-IR systems are generally used to monitor well-defined environments. Also, extractive FT-IR systems monitor the same optical path for every application, and most importantly, the optical path in extractive FT-IR systems can be purged with nitrogen gas to generate excellent background single-

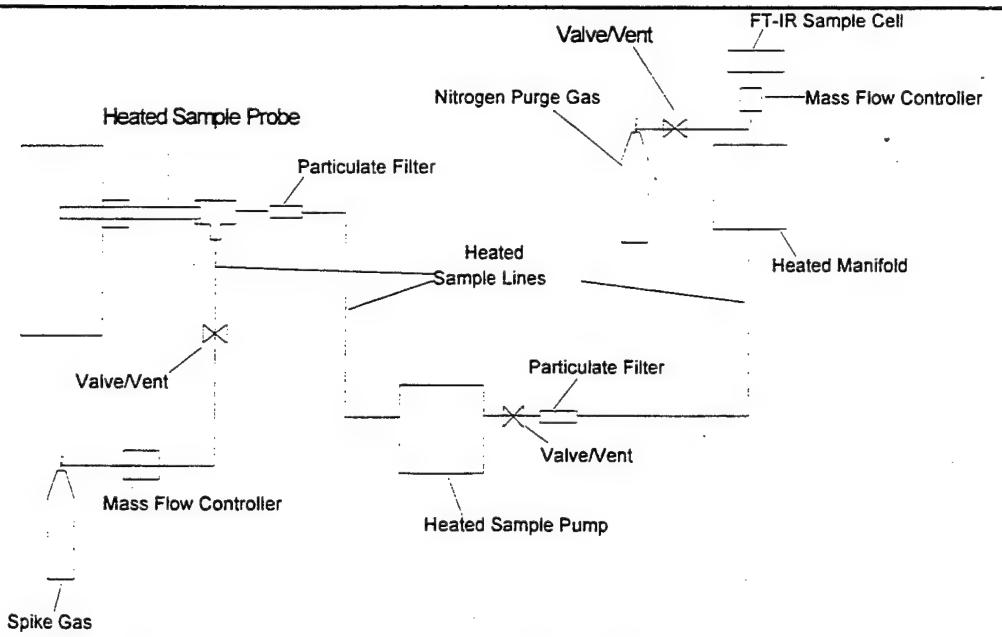

Figure I.C.3. A sampling system for use in extractive FT-IR monitoring, using a heated manifold and capable of supporting the use of analyte spikes.

beam spectra. Extractive systems allow the analyst to control the conditions within the sample space; appropriate choice of the parameters associated with the sample space conditions can greatly improve the outcome of an extractive FT-IR analysis.

Temperature may be the most important data collection parameter, for two reasons. First, as previously discussed, the sample temperature must be high enough to prevent hot gases in the sample from condensing in the sampling system. Second, sample temperature is important because the band shape of infrared absorbance bands are temperature dependent.

It is also important that the reference spectra used in the analysis of extractive FT-IR monitoring data be collected at the same temperature as the field spectra. Temperature-induced band shape differences in field spectra and reference spectra will prevent the spectral interpretation algorithm (be it manual or automated) from accurately characterizing the field spectra. Evidence of such spectral band shape mis-matches due to different temperatures may become evident in high spectral resolution data for some compounds displaying narrow line structure when the temperature differences are as little as 10° C. While the use of lower spectral resolution and broader analyte bands may visually mask the problem until temperature differences become much greater, the effects are probably still present at similarly low temperature differentials. The effect of these mis-matches on analytical accuracy has not been well-characterized; simply matching the temperature of the reference spectra to the sample spectra eliminates uncertainty in this regard.

The amount of time to purge between samples of different composition (e.g., sample gas and nitrogen blank gas) will depend on the cell volume, cell flow characteristics, and the flow rate of the sampling system being used in any given application. A cell that displays plug flow may be fairly well purged after only three cell volumes have flowed through it. (For example, a 4 liter cell would be purged after 12 liters of gas has been flowed through it. If the flow rate of the system is 2 liters per minute, then the purge time would be 6 minutes.) Other cells may require considerably longer purge times; the EPA extractive FT-IR protocol (1) suggests 10 cell volumes are necessary. Perhaps the best approach is to use spectral analysis of cell samples during purging to provide evidence of satisfactory purge times.

Multiple considerations determine the data collection time to be used for each spectrum. First, the SNR that is required to successfully monitor any given application provides a minimum for coaddition time. The SNR that is required can be estimated from either the analyte level that is expected in the sample, if the monitoring is done for survey purposes, or the minimum analyte level of interest for regulatory- or safety-oriented monitoring. Because the optical path does not change and because the cell can be purged to collect a background spectrum, actual detection limits may approach ideal detection limits in extractive FT-IR applications (except for cases involving complex matrices

with many interferents). This allows a minimum SNR to be accurately determined before the field work is performed. The collection time should then be set to produce at least this SNR.

If the minimum required SNR can be achieved with relatively short coaddition times, the analyst may still want to consider lengthening the coaddition times based on the goals of the monitoring project and the nature of the process being monitored. For example, if the monitoring is being performed to specifically detect chemical events that change rapidly with time, then the minimum collection time determined earlier to produce adequate SNR may be the best coaddition time to use. However, if the goal of the monitoring is to track the concentration of analytes over long periods of time during which the concentration should not change rapidly, longer collection times may be used to minimize data analysis and data storage concerns.

Various other parameters involving the FT-IR instrumentation may also be user-selected. Perhaps the most significant is spectral resolution. The best spectral resolution to use in monitoring any given analyte strongly depends on both the line width of the analyte absorbance bands and the method of data analysis that will be employed to interpret the sample spectra. When monitoring compounds that display narrow band width, higher resolution will afford a more detailed spectrum that is easier to analyze by the human eye. However, if automated spectral interpretation algorithms are to be used, lower resolution spectra may provide a sufficiently accurate analysis.(7,8) If the compounds to be monitored have broad absorbance bands, high resolution spectra will not afford any advantage even when interpreting the spectra manually. In general, the resolution of choice should be the lowest resolution that will provide a satisfactory analysis of the sample spectra.

The apodization function used is often user-selectable and either a boxcar or triangular apodization function is typically selected. The choice of apodization function is not nearly as important as ensuring that the same function is used in the collection of the field spectra that was or will be used in the generation of the library reference spectra used for quantitative analysis.

The collection of the background spectrum in extractive FT-IR monitoring is straightforward. Because extractive FT-IR systems use a closed cell, the cell can be purged with nitrogen for collection of the background spectrum. This background collection should be performed using the same collection parameters used to obtain sample spectra, and the process should be repeated as often as necessary to maintain good baselines in the sample absorbance spectra.

I.D. An introduction to FT-IR spectral interpretation and data reduction

The methodologies presented in this section are based on the experience of the AeroSurvey and generally follow procedures outlined in two ASTM documents that deal with the interpretation of FT-IR spectral data: "Standard Practice for General Techniques for Qualitative Infrared Analysis" (ASTM document E 1252 - 94) and "Standard Practice for General Techniques of Infrared Quantitative Analysis" (ASTM document E 168 - 92).(25,26)

I.D.1 Qualitative analysis of spectra

Although much attention has been given to the development of methodologies and automated algorithms for the quantitative analysis of FT-IR spectra, these methodologies generally fail unless an accurate qualitative assessment of the spectral components has been made.(13) Unfortunately, the qualitative interpretation of spectra can be quite difficult, especially for users with little or no experience in atmospheric infrared spectroscopy.

Essentially, qualitative analysis of air samples is accomplished by detecting and identifying either the analyte's absorption bands in transmittance spectra or the analyte's absorbance bands in absorbance spectra. Spectral libraries, printed and in digitized form, are available to help with the identification of spectral bands but identification can still be a daunting task, as the number of possible infrared active compounds is immense.

In practice, knowledge of the site or activities that produced the analyzed air sample allows the vast majority of potential compounds to be safely eliminated from consideration. Compounds with poor volatility are rarely seen in most ambient FT-IR spectra, unless the spectra were collected directly over an area of active release.

The general location of an absorption band in the infrared spectrum is often explained in terms of functional group frequencies and knowledge of group frequencies can aid considerably in qualitative analysis. Basically, different compounds with similar functional groups will usually display bands in certain regions of the infrared. Ketones, for example, display bands in the 1600 cm^{-1} - 1800 cm^{-1} region. Similarly, bands around 3000 cm-1 are usually due to carbon-hydrogen bond stretching, suggesting the presence of hydrocarbons.(14)

I.D.2 *Quantitative analysis of spectra based on absorbance band intensity*

In a conventional absorbance spectrum, the presence of an infrared-active compound in the sample single-beam spectrum results in a positive absorbance peak. The intensity of the band is linearly related to concentration, through a

relationship expressed by Beers law:

$$A = abc$$

where

A = absorbance value
a = an absorption coefficient which is dependent upon compound, frequency, instrumental effects, and (to a lesser degree) temperature and pressure
b = the infrared beam path length through the sample
c = the concentration of the compound in the sample

As stated earlier, the amount of the infrared light absorbed by a sample depends on the amount of compound present in the sample. *Reference spectra* can be created by introducing prepared samples of known concentration into the infrared beam. (Although it is common to hear the background spectrum referred to as the reference spectrum, such terminology can result in some confusion. The term *reference spectrum* is less ambiguously used to describe an absorbance spectrum of an analyte at a known composition that can be used as a reference point for qualitative and/or quantitative analysis of spectra of samples with unknown composition.)

Real-world sample spectra often display the bands of more than one infrared active compound and the bands may overlap. Within the limits of Beer's law linearity, overlapping band intensities are essentially additive, with the composite band in the actual recorded spectrum being the cumulative result of the individual bands that comprise it. In mathematical terms, the actual absorbance spectrum is a linear combination of the absorbance spectra for each pure component of the sample in the beam.

Algorithms exist that can analyze complex spectra by capitalizing on the linear nature of the absorption bands' intensities. *Classical least squares* (CLS) routines attempt to minimize the difference, or *residual,* spectrum present after subtraction of a model spectrum from the actual spectrum to be analyzed, when the model spectrum has been "synthesized" from reference, or *library,* spectra.

Variations on CLS exist, such as Partial Least Squares (PALS) and Principle Component Regression (PER). These methods represent alternative mathematical approaches to automatically interpreting complex spectra and each one offers certain advantages and disadvantages. (See reference 2, pp. 362-366.)

The greatest disadvantage to all of these automated algorithms for quantitatively analyzing spectra is that they require knowledge of all significant components of the spectra to function properly and produce reliable results.(13) This requirement is often difficult to meet in environmental spectra, at least initially. However, when all potential spectral components are known and appropriate-temperature reference

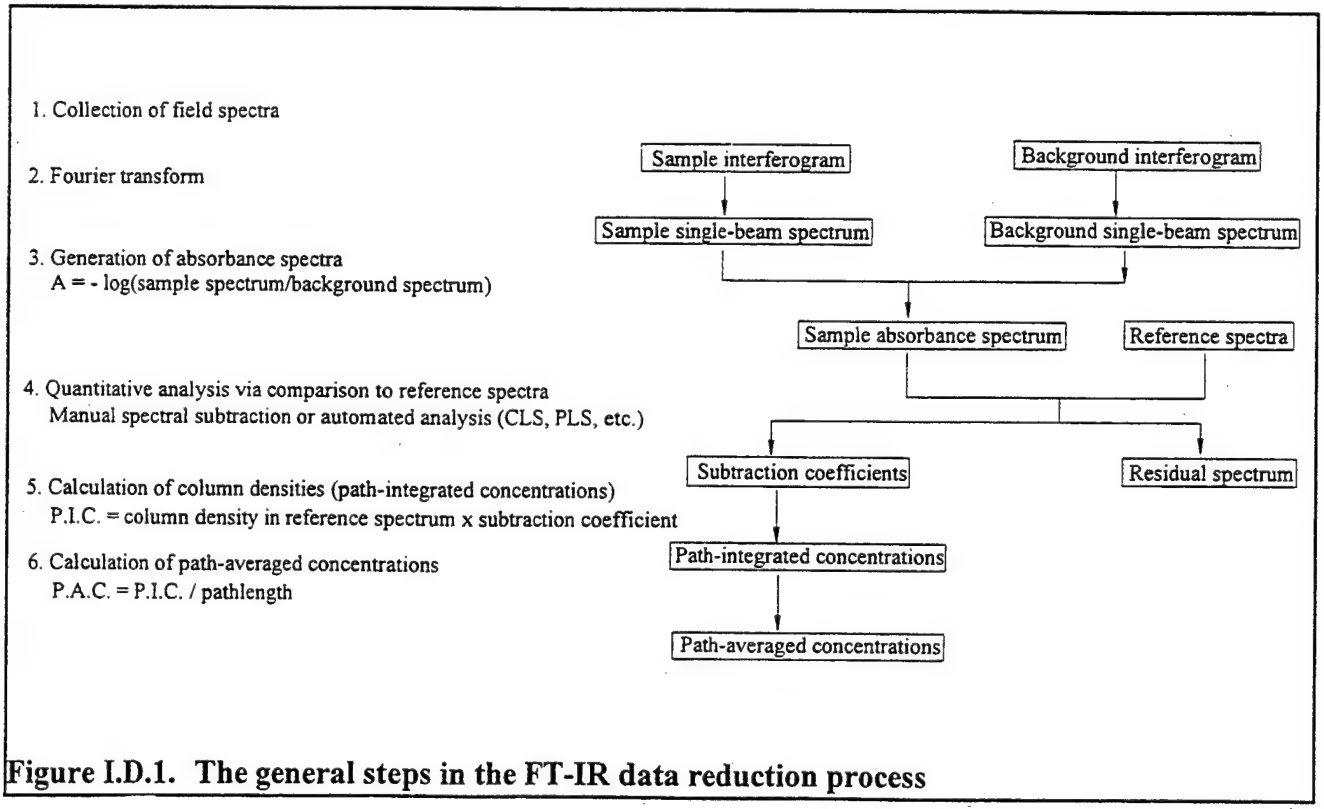

Figure I.D.1. The general steps in the FT-IR data reduction process

spectra of each component are available, automated algorithms can be successfully implemented in many FT-IR air monitoring applications.

Another limitation of these algorithms is that they are often limited in terms of the maximum number of components (usually around 20) that may be included in the library when the algorithm is run on current-generation PC computers. Future software and hardware developments should improve this for PC users. While users of more powerful computers may not experience this limitation, they may have difficulty finding commercially available software to perform these types of spectral analyses directly.

As previously discussed, accurate characterization of a field spectrum can only be achieved in the context of reference spectra collected at the same temperature as the field spectra. Automated spectral interpretation routines are especially sensitive to widely differing temperature conditions in the field spectra and the library reference spectra. Examples of the latter problem have been seen in FT-IR spectra collected at a landfill and analyzed for methane concentrations. Methane values from the automated interpretation algorithm were not consistent with other data and the detection limits in general were found to be much worse than anticipated. A visual examination of the absorbance spectra revealed that the methane bands in the field spectra, which dominated the spectra after carbon dioxide and water, did not match the appearance of methane bands in typical library reference spectra collected at laboratory temperatures. Documentation accompanying the data even reported that the methane being measured was escaping from vents at 65° C but failure to consider the difference between sampling temperature in the reference and field data resulted in an unsatisfactory performance. The methane data could be post-analyzed with better results by using a methane reference spectrum collected at a temperature that more closely matched the temperature of the methane in the field.

I.D.3 FT-IR spectral interpretation and data reduction - An illustrated overview

Figure I.D.1 summarizes the process of generating information from FT-IR data via quantitative analysis of bands in absorbance spectra. Most FT-IR spectrometers used for air analysis are not dual-beam instruments in the traditional sense. True dual beam spectrometers have two beam paths, one for the sample and one for the background. In these instruments, both beams are detected and radioed simultaneously to

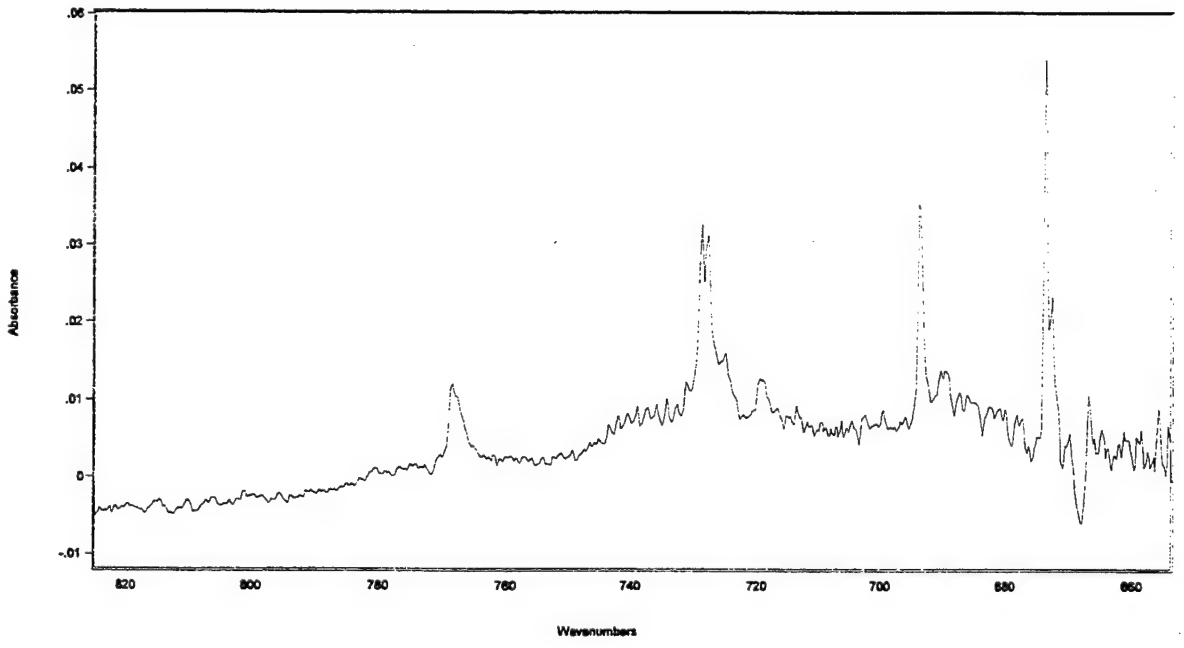

Figure I.D.2. A portion of an open-path FT-IR absorbance spectrum, displaying various analyte and atmospheric interference bands.

produce dual-beam spectra directly. In FT-IR air monitoring, dual beam spectra (absorbance spectra) can only be created by ratioing sample and background spectra collected at different times.

Once absorbance spectra have been created, qualitative interpretation of the bands in the spectrum is necessary. Even if an automated algorithm is to be used in the quantitative analysis of the analyte bands, a qualitative analysis mustfirst be performed to identify all of the major components of the spectrum. As stated earlier, this part of the data reduction process may be the most difficult for novice users. Figure I.D.2 is an open-path FT-IR absorbance spectrum collected over a 100 meter pathlength, displaying bands from a number of different compounds

Fortunately, a modicum of experience allows most users to recognize the ever present water and carbon dioxide bands. Most (but certainly not all) analyte bands are broader than those produced by the atmospheric interferents. The compounds represented in the spectrum shown in Figure I.D.2 all possess bands with rather sharp peaks atop broader bases. At low concentrations, it is the sharp peaks that are most visually apparent.

Negative peaks in absorbance spectra usually indicate a compound was in greater concentration in the background spectrum than in the sample spectrum. Negative analyte bands indicate the single-beam spectrum chosen as the background was a poor choice, as it was apparently collected when more analyte was present in the beam path than was present during the collection of the sample spectrum. Often, negative bands are due to atmospheric carbon dioxide or water, as is the case with the CO_2 feature at 667 cm^{-1} in Figure I.D.2.

Following the identification of the major bands in an absorbance spectrum, quantitative analysis can be performed based on the appropriate library reference spectra. The analyte reference spectra pertinent to the absorbance spectrum in Figure I.D.2 are shown in Figure I.D.3. These are the same analytes chosen to illustrate the effects of overlapping bands from multiple analytes in Figure I.A.3 earlier. Notice how the noise-free composite spectrum in Figure I.A.3 has a different appearance than the actual field spectrum in Figure I.D.2. This difference is partially due to lower analyte concentrations and different relative analyte proportions in Figure I.D.2 compared to Figure I.A.3. However, it is the presence of additional instrumental noise (in the form of a non-zero baseline and increasing noise due to low signal response) and chemical noise (in the form of spectral features due to absorption phenomena associated with atmospheric carbon dioxide) that account for most of the difference in appearance. Recognition of analyte peaks among the various spectral features due to the atmospheric interferences can be difficult for users unfamiliar with infrared spectra of air.

The top spectrum in Figure I.D.4 is the result of subtracting the benzene reference spectrum from the sample absorbance spectrum in Figure I.D.2. Direct subtraction of a reference spectrum from a field spectrum will almost always

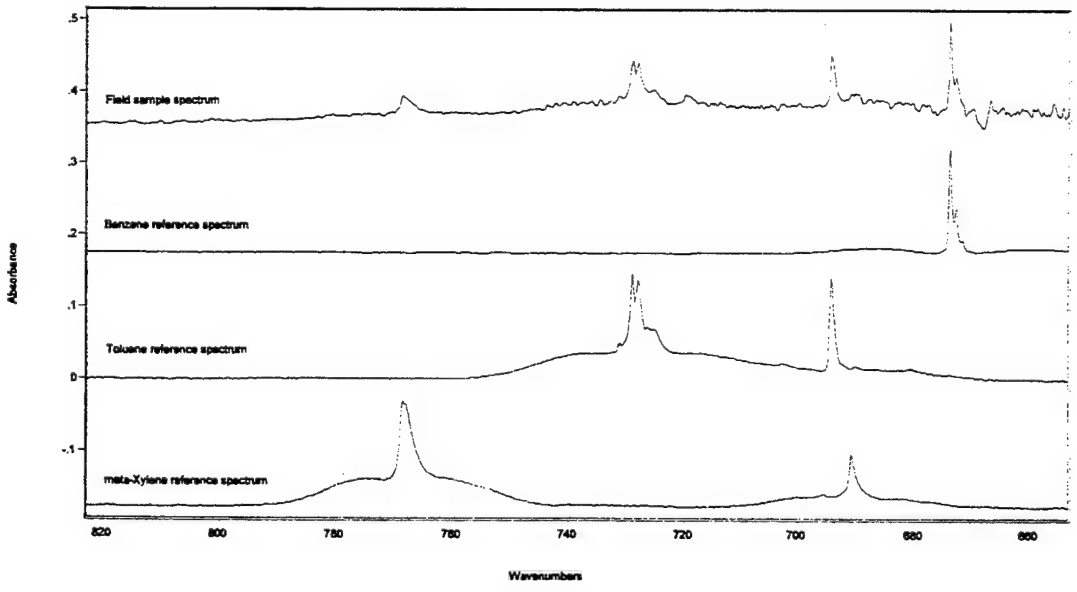

Figure I.D.3. The field absorbance spectrum from Figure I.D.2, with relevant reference spectra.

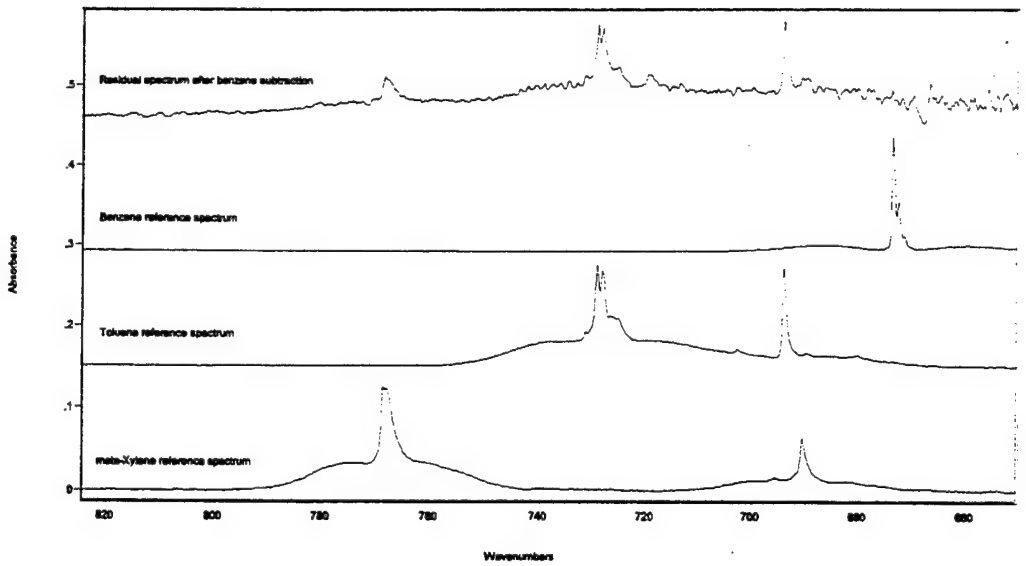

Figure I.D.4. The residual spectrum (top) remaining after the subtraction of the benzene reference spectrum from the field absorbance spectrum in Figures I.D.2 and I.D.3 overlaid with reference spectra of benzene, toluene, and meta-xylene.

result in under- or over-subtraction of the analyte signature because of different band intensities in the field and reference spectra. To effect perfect *stripping* of an analyte band from a field spectrum, the appropriate reference spectrum is multiplied by a scaling factor. When quantitative analysis of spectra is performed manually, the value of the scaling factor is adjusted while viewing the resultant (or *residual*) spectrum, allowing an interactive subtraction of the analyte's bands from the sample spectrum. In the simplest sense, automated algorithms for the quantitative analysis work the same thing, except that the scaling factors are determined mathematically for all reference spectra simultaneously to produce the lowest possible baseline variations in the residual spectrum.

Figure I.D.5 shows the final residual spectrum after all of the analyte components have been manually stripped out. The residual peak at 720 cm^{-1} is due to a carbon dioxide (a non-fundamental "hot" band), as are many of the other residual features in the spectrum. Small features in the residual baseline suggest that minor quantities of some other, unidentified analyte may have been present in the sample space. The intensities of these bands are too low to allow identification and quantitative analysis.

The actual detection limit for any analyte in a given spectrum is related to the noise in the spectrum over the regions relevant to that analyte, whether or not that analyte is actually detectable in the spectrum. Detection limits are often calculated as the amount of analyte necessary to produce an absorbance peak intensity of at least three times the peak-to-peak noise level.

It should be noted that the spectrum in Figure I.D.2 was analyzed without stripping of the water and carbon dioxide bands. Although some atmospheric interferant bands overlapped the analyte bands, manual interactive stripping still worked because the ability to determine the underlying baseline was not impaired. These interfering bands would, however, impair the ability of an automated analysis algorithm unless reference spectra were provided that allowed the atmospheric bands to be accurately stripped as well. Nearer the edges of the windows of atmospheric transmission, interfering bands may become more of a problem, even with a manual stripping approach. Removal of some of the carbon dioxide features from the field spectrum shown in Figure I.D.2 could have resulted in less noise in the residual spectrum and accordingly improved sensitivity and detection limits for the analytes measured.

Reference spectra that accurately model the appearance of carbon dioxide and water in atmospheric spectra are extremely difficult to generate. Because of the relatively large amount of carbon dioxide and water in air,

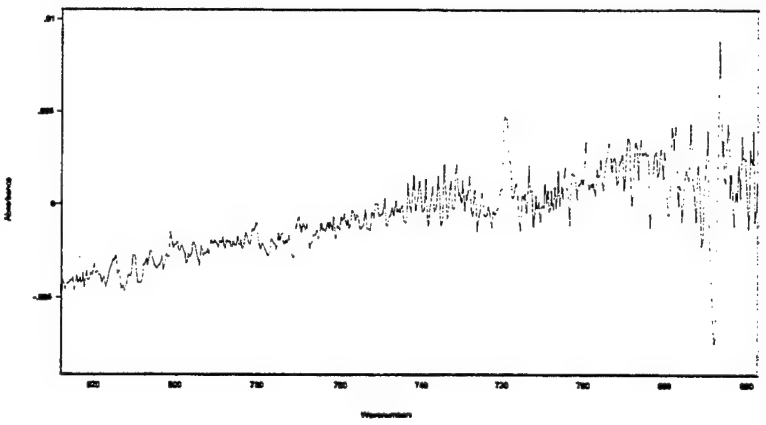

Figure I.D.5. The final residual spectrum after all identified analytes have been stripped from the field absorbance spectrum shown in Figure I.A.2. Many of the residual features in this spectrum, including the peak at 720 cm^{-1}, are due to carbon dioxide that has not been stripped from the field spectrum. Notice the difference in scale on the ordinate axis compared to the original field spectrum before spectral subtraction.

strong fundamental bands due to these compounds are distorted over even short beam paths. Additionally, high column densities can cause weak overtone bands to appear strongly in atmospheric spectra and the appearance of these bands is extremely temperature dependent. The result is that no single reference spectrum for carbon dioxide or water is likely to accurately strip out all relevant interfering bands. The residual spectrum in Figure I.D.5 is an excellent example of this problem. The upward-pointing band at 720 cm^{-1} is due to carbon dioxide as is the downward-pointing feature at 667 cm^{-1}, an apparent paradox that cannot be modelled by any single carbon dioxide reference spectrum.

To complete the data reduction process, the column density values associated with each analyte reference spectrum are multiplied by the subtraction factors required to strip the bands from the spectrum (or the equivalent coefficients produced by an automated algorithm), producing column density values for each analyte measured in the spectrum. The data may be further adjusted to account for temperature, pressure, and pathlength.

I.E. References

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(10) G.M. Plummer, and co-workers, "Field Applications of FTIR (Fourier Transform Infrared) Spectroscopy for Detection of Hazardous Air Pollutants at Industrial Sources", *Air Pollution Measurement Methods and Monitoring Studies, Vol 3a* (Proceedings of the Annual Meeting of the Air and Waste Management Association, 87), Paper No. 94-RP129.05.
(11) C.M. Nelson, and co-workers, Proceedings of the 11th Annual International Pittsburgh Coal Conference, 1994 (Vol. 1) pp. 524-529.
(12) "Pocket Guide to Chemical Hazards" National Institute for Occupational Safety and Health, Publication # 90-117, pg. 60 (1990).
(13) P.Saarinen, J. Kauppinen, "Multi-Component Analysis of FT-IR Spectra", *Applied Spectroscopy*, **45**(6), pp. 953-963, (1991).
(14) D. Lin-Vien, and co-workers, "Infrared and Raman Characteristic Frequencies of Organic Molecules", Academic Press (1991).

Other resources

Current versions of EPA documents describing protocols for various FT-IR air monitoring applications can be accessed through the Internet. The relevant bulletin boards may be accessed by telnet'ing to TTNBBS.RTPNC.EPA.GOV or documents may be downloaded from a similar Web site, www.rtpnc.epa.gov. Of particular relevance to this chapter are the AMTIC (Ambient Monitoring Technical Information Center) and EMTIC (Emissions Monitoring Technical Information Center).

II. System hardware

This section describes the hardware components of the FT-IR system constructed by AeroSurvey, Inc. and delivered to the U.S. Army ERDEC in November 1997, under contract DAAD-97-P-3045. As the system was intended for applications in the demilitarization effort, we refer to the instrument as the ASI/Demil FT-IR system for the purposes of this document.

The ASI/Demil FT-IR system is constructed around FT-IR componentry originally produced by Midac Corporation (Irvine CA). The FT-IR componentry was salvaged from a FT-IR system custom built by Apogee Scientific under a previous U.S. Government contract. In the project documented herein, the FT-IR components have essentially been reconfigured into a purgeable enclosure.

The enclosure has been specially designed to interface with a multipass infrared gas cell - specifically, a variable pathlength cell originally produced by Infrared Analysis (Anaheim, CA) and owned by Midwest Research Institute (Kansas City, MO). However, the design of the enclosure includes considerations for future applications of the FT-IR system that may involve various sampling peripherals in addition to or in place of the particular multipass gas cell with which the FT-IR system was delivered.

II.A Enclosure

The ASI/Demil system enclosure is diagrammed below in Figure II.A. The enclosure is divided into three internal compartments. The interferometer compartment (on the right end of the enclosure when viewed from the front) contains the actual interferometer engine, the infrared source assembly, and associated electronics. On the left end of the enclosure, the detector compartment contains the detector assembly and laser alignment assembly (used to align the multipass gas cell). The center sample from the interferometer compartment to the detector compartment.

The interferometer and detector compartments are accessed through cover plates on the top of the enclosure. The sampling compartment can be accessed either from the top of the enclosure if the gas cell is not mounted atop the case or from the bottom via an access plate. For wide open access during configuration of alternative sampling systems, both the front and rear sides of the enclosure may be removed without disturbing the multipass gas cell mounting arrangement or the optical alignment of the FT-IR components.

The top and bottom access plates are o-ringed to provide a positive seal for purging during operation. Purge gases enter the case via two ports, one on each end of the case. The ports are tapped for 1/8" NPT fittings. The instrument has been originally outfitted with ¼" Swagelok fittings.

II.B Midac FT-IR componentry

The interferometer engine, infrared source assembly, detector assembly, and associated power supply and data acquisition electronics were originally components of a Midac air monitoring spectrometer, Model M2500-C, serial #189, manufactured in November of 1994.

II.B.1 Source assembly

The source assembly consists of an infrared source, an off-axis parabolic mirror, and the mount. The infrared source is a resistive heating element made of silicon carbide (SiC). The SiC source (sometimes termed a *glower*) glows orange when powered and emits broadband radiation across the infrared spectrum.

The infrared source is operated at a nominal 12 VDC. Power is supplied by the power supply board located behind the interferometer engine. A voltage regulator is

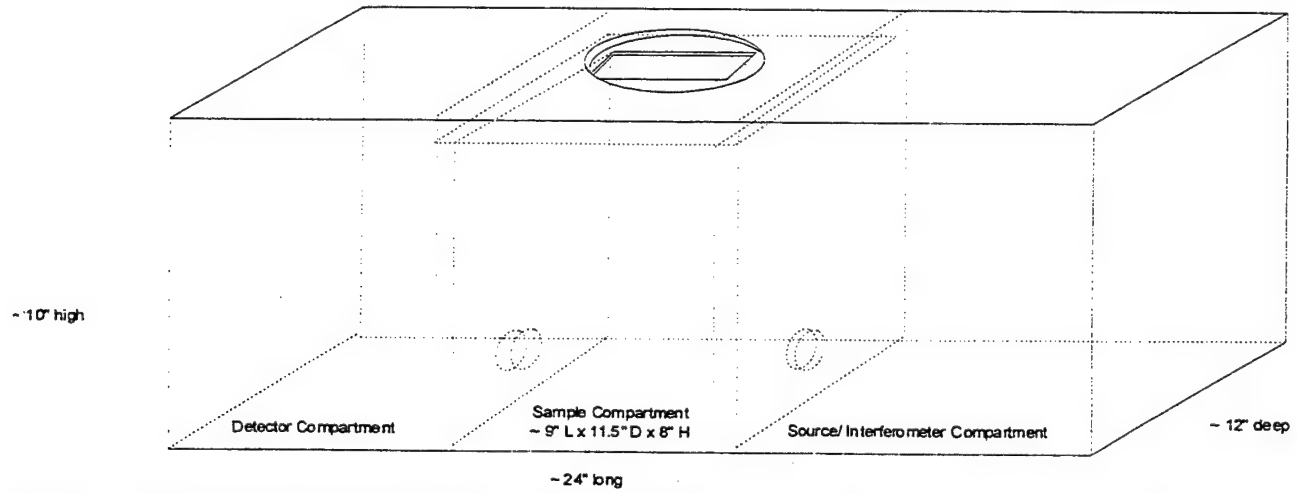


Figure II.A **Configuration and approximate dimensions of the enclosure constructed for the ASI/Demil FT-IR system.**

interferometer compartment. The infrared source element pulls about 2 amps of current.

The source assembly's mount positions the infrared glower at the focal point of the off-axis parabolic mirror. The mirror thus collimates the light emitted by the source and sends the collimated beam of broadband infrared light into the interferometer engine for modulation.

II.B.2 Interferometer engine

The interferometer engine modulates the broadband infrared light beam and sends the modulated beam through the sample compartment and to the detector compartment. For an explanation of interferometer operation, see the previous section entitled "Basic FT-IR Theory, Operation, and Design".

The Midac M2500-C interferometer is capable of 0.5 cm-1 resolution. The ZnSe beamsplitter and MCT detector in this particular unit afford response from 650 cm-1 to over 5000 cm-1. (Note: The unit's original model number, M2500-C, is deceiving, in that it denotes a system with a KBr beamsplitter. Although labeling on the interferometer body also indicates the presence of KBr optics, it in fact contains a ZnSe beamsplitter. The interferometer has evidently been retrofitted with the more desirable, non-hygroscopic ZnSe beamsplitter at some point in its history.)

A HeNe laser is mounted to the top of the interferometer engine. A small prism introduces the HeNe laser beam into the interferometer. Two small detectors mounted on the interferometer engine monitor the modulated HeNe laser signal. The signal from these two laser detectors is used as a feedback mechanism for control of the interferometer's moving mirror. *This interferometer-mounted laser should not be confused with the laser assembly used for optical alignment of the multipass gas cell. The laser used for gas cell alignment is a small diode laser mounted in the detector compartment.*

II.B.3 Detector assembly

The detector assembly consists of a liquid nitrogen dewar containing an infrared detector, an off-axis parabolic mirror, a preamplifier on a small printed circuit board, and the mount.

The modulated light beam coming from the interferometer is collimated when it enters the detector compartment. The off-axis parabolic mirror in the detector assembly focuses this collimated beam onto the actual detector element. The detector element is small chip of mercury-cadmium-telluride (MCT) material, positioned on the end of a cold-finger within the liquid nitrogen dewar. Liquid nitrogen is added to an inner chamber within the dewar from a filling hole on top of the dewar. The cold finger upon which the detector chip is mounted extends into an evacuated region between the inner and outer walls of the dewar. An infrared-transparent window in the side of the dewar allows infrared light to enter the evacuated dewar and impinge on the detector.

Dewars sometimes lose their vacuum seal, allowing ambient air to leak into the inner space of the dewar. Water in the air will then condense when the detector is first cooled with liquid nitrogen, and this condensed water will degrade the quality of the spectra collected. See the following troubleshooting section for more information on diagnosing and correcting this problem.

The MCT detector produces a small electrical signal in response to the modulated infrared light that strikes it. A pre-amplifier mounted on the detector assembly increases the intensity of the signal. The amount of gain in the pre-amplifier is determined by the placement of jumpers on a series of eight pins labeled "A" through "H". Jumpering pins "A" produces the least amount of gain (for high light levels). Jumpering pins "H" produces the greatest amount of gain (for low light levels).

(Note: There are three pins for each gain setting. The two pins closest to the middle of the pre-amplifier board must be jumpered to activate that gain setting. The pins nearest to the edge of the pre-amplifier are inactive.)

II.B.4 Associated on-board electronics

Two printed circuit boards, the digital mirror drive board and the analog mirror drive board, are attached to the interferometer engine. These boards are responsible for accurately driving the interferometer's moving mirror, based on the feedback from the modulated HeNe laser signal. Jumpers placed on pins found along the top edge of the digital mirror drive board control various aspects of the interferometer's operation, such as mirror velocity, laser sampling rate, etc. *These jumpers should only be changed by personnel familiar with their function and the implications of changing them.*

Behind the interferometer engine, two printed circuit boards are mounted on a bracket that is in turn attached to the side of the enclosure. The rear-most printed circuit board is the power supply board. Taking twelve volts from an external power supply, this board supplies various voltages to the other FT-IR components. The 12 VDC input is fed into the power supply board via screw-down terminals on the top edge of the board. The same terminals are used as a source of 12 VDC power for the infrared source assembly and the cell alignment laser assembly.

The printed circuit board nearest to the interferometer engine is the analog-to-digital converter (ADC). The ADC board receives the signal from the detector preamplifier, filters it to remove unwanted signal (due to electrical and mechanical noise within the system), and converts it to a digitized signal that is then sent to the computer.

II.C Laser alignment assembly

The laser alignment assembly was custom-designed for this instrument and is built around a small diode laser. The diode laser is ultimately takes power from the 12 VDC supply on the power supply board. The voltage supplied to the laser diode is dropped to 5 VDC by a voltage regulator located in the detector compartment.

The laser beam is sent to a small pick-off mirror, which then directs the beam into the sample compartment. The pick-off mirror occludes a small portion of the infrared beam. This signal loss was found through experimentation to have no discernable effect on the performance of the instrument. For this reason, the laser alignment system is permanently mounted to provide greater reliability and ease of implementation.

Small diode lasers are prone to overheating. To avoid permanently damaging the laser diode, it is recommended that the laser not be left on indefinitely during data collection. A switch on the left end of the enclosure is available for turning the alignment laser on and off.

II.D Multipass infrared gas cell

As originally delivered the FT-IR system was configured around a particular multipass infrared gas cell provided by Midwest Research Institute. It is likely that the FT-IR system may be used with other sampling systems and, in fact, the enclosure has been designed with future alternative applications in mind. Nonetheless, in the interest of completeness, this section will specifically address the particular cell with which the system was originally delivered.

The cell was originally produced by Infrared Analysis (Anaheim, Ca.) as part number 35-V. It is a glass-bodied cell with a 5" I.D. and a volume of approximately 8.5 liters. The base path between the upper and lower set of mirrors is approximately 22". The minimum pathlength through the cell is approximately 88" (two round trips) and the pathlength increases in increments of 44" as the mirrors are adjusted to result in multiple reflections.

The configuration of the mirrors in the gas cell affords multiple reflections with minimum signal loss through an innovative optical design. The optical design was originally described by J.U. White in a 1942 paper (Long Optical Paths of Large aperture", Journal of the Optical Society of America, 32, 85) and such cells are often referred to as White cells.

II.D.1 Gas cell transfer optics

A box attached to the end of the gas cell contains the transfer optics. The purpose of the transfer optics is to intercept the collimated beam passing through the sample compartment, send it into the cell to be reflected between the cell's mirrors, and then return it to sampling compartment to be passed on to the detector compartment.

The cell's transfer optics consist of two off-axis parabolic mirrors. The first mirror folds the beam 90 degrees and introduces it into the cell. The second mirror folds the exiting beam back into the original path, toward the detector compartment.

II.D.2 Cell internal optics.

The cell's internal optics consist of three mirrors – two at the top and one at the bottom of the cell as it is mounted on the ASI/Demil system. The mirrors are configured so that a diverging beam striking one of the top mirrors is returned to a focus on the bottom mirror, which then returns the re-diverging beam back to the other top mirror. This process is repeated, with each round trip producing a new focal point on the bottom mirror, until one of the focal points misses the bottom mirror and escapes. When the mirrors are properly set, adjustment of only one of the first top mirrors allows the number of passes to be determined.

II.E. Sample monitoring instrumentation

Accuracy in FT-IR gas monitoring is directly related to knowledge of the sample's temperature and pressure. Knowledge of flow is also useful for extractive (cell-based) systems in that it allows purge times to be verified once for any given sampling set-up and then satisfactorily repeated without future re-calibrations.

The ASI/Demil FT-IR system has been delivered with a flow sensor capable of also reporting pressure and temperature (Model PVU-10SLPM-S, Alicat Scientific, Tucson, AZ). This sensor should be satisfactory for all measurements of low-flow gas streams at or near room temperatures. High temperature measurements will require a separate temperature sensor, preferably located in the cell.

The pressure sensor within the Alicat unit measures the pressure at the *input* of the sensor. Therefore, the sensor should be installed on the cell *output* port in order to infer cell pressures most directly and accurately. However, the Alicat unit is only rated to 50 C and use of the sensor on the output port with streams heated above 50 C is not recommended.

Considering the temperature limitations of the sensor and the fact that temperature is best measured by an in-cell sensor in all cases, AeroSurvey is recommending that the Alicat sensor be used on the cell's input port. The pressure drop across the unit is approximately 15 torr at full flow. Based on this value, maximum error in the measurement of the cell's pressure due to the pressure drop across the flow meter should be less than 2%. The error should be considerably less at the 3 SLPM rate used to collect the validation data supplied with ASI/Demil system.

Flow restrictions between the sensor and the cell should be minimized regardless of the location of the sensor relative to the cell's input and output ports.

In testing, it was discovered that the sensor begins to read inordinately high temperatures when the internal 9 V VDC battery nears discharge. Increasing temperature readings may indicate the need for a fresh battery.

II.F. System alignment

Alignment of any optical system requires patience and is facilitated by a thorough understanding of the optical train. Although the procedures for aligning this system are presented below in a step-by-step fashion, an iterative approach is usually required to achieve optimal alignment.

During a non-critical time when the system is in good alignment, personnel responsible for data collection should experiment with the various elements of the system. It is important to gain an understanding of how the alignment of each element in the optical train affects the instrument's response.

AeroSurvey recommends viewing single-beam spectra in real-time during all alignment procedures and alignment experimentation. Always view the infrared spectra from 0 cm-1 to 8000 cm-1 when aligning or trouble-shooting instrument problems. Many spectral indicators of alignment and instrument health in general can be seen in the this broad region but not necessarily in the narrow analytical regions that are sometimes employed during analysis.

II.F.1 Optical alignment of the cell

A comprehensive alignment of the cell optics proceeds in a number of steps:

Step 1. Rough alignment of the cell's internal optics (cell disassembled, mounted or dismounted)
Step 2. Rough alignment of the cell's transfer optics (cell assembled but dismounted)
Step 3. Rough alignment of the cell's top mirror to produce the number of passes desired (cell mounted)
Step 4. Fine alignment of the cell's top mirror/double check number of passes (cell mounted)
Step 5. Fine alignment of the cell's transfer (cell mounted)

Only step 4 is routinely required. The cell's alignment is remarkably stable, even after the cell has been removed from and replaced to it's mounting position atop the instrument. Alignment procedures beyond the scope of step 4 should only be required if the cell has been subjected to severe vibration during transportation, completely disassembled, or grossly misaligned.

In particular, steps 3 and 4 are required whenever the pathlength is changed. Steps 1,2, and 5 may be needed after a complete breakdown of the cell for cleaning or inspection. As a rule, the last three steps should be performed any time the first two steps have been performed.

Cell alignment step 1:
Rough alignment of the cell's internal optics with the cell disassembled

Arms extending from the cell's bottom plate support the top mirrors. The cell's top end plate may therefore be removed without disturbing the internal mirror assemblies. Likewise, the cell's glass cylinder may be removed without disturbing the cell's alignment. In fact, the cell can be operated quite effectively as an ambient air monitor with the glass cylinder removed.

With top plate and glass cylinder removed, the mirror assemblies may be roughly aligned by simply ensuring that their back surfaces are approximately parallel to the mounting plate.

Cell alignment step 2:
Rough alignment of the cell's transfer optics with the cell dismounted from the enclosure

With the cell off of the FT-IR enclosure and on the floor or a bench, the transfer optics may be brought into rough alignment. The transfer optic mirrors are each adjusted with a set of three screws extending out the bottom of the transfer optics box. The middle screw in each set of three must be loosened to allow adjustment. The middle two outside screws in each set of three actually adjust the mirrors' orientations.

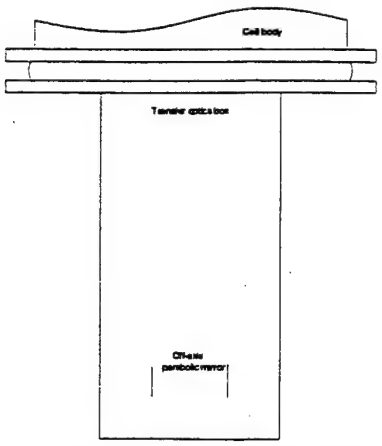
Rough alignment of these mirrors can be achieved with a "visual centering" technique. With this technique, one looks into each side of the transfer optics box and adjusts the mirror being viewed so that the entrance window into the cell is centered in the image seen in the mirror.

For this technique to work well, one's view into the transfer optics box must be square with respect to the transfer optics box. This can be achieved by looking into the box at arm's length with only one eye and ensuring that the circular silhouette of the mirror surface is evenly framed by the hole exiting the other side of the box. See Figure II.F.1.b.

When reassembled after steps 1 and 2, the cell should be sufficiently aligned to allow light to pass through it and the FT-IR system to operate.

Cell alignment step 3:
Rough alignment of the cell's top mirror to produce the number of passes desired

With the cell's internal mirrors and transfer optics in at least a rough alignment, the external adjustment screws may be used to align the first top mirror such that the desired number of reflections within the cell results. A



Note circular silhouette of mirror face is evenly framed in the hole on the transfer optic box. Rear mirror is completely occluded by the front mirror.

Figure II.F.1.b. Appearance of transfer optics box when viewed squarely.

red diode laser is used to provide an intense visible light beam so that the number of passes may be visually determined, via a count of the red dots produced on the bottom mirror by the multiple reflections.

This in turn requires a quick check of the laser assembly alignment. This is accomplished by removing the cell assembly and simply ensuring that the laser beam is passing through the center of both circular ports separating the three compartments of the enclosure. A white card or piece of paper placed in front of each port facilitates location of the beam.

Once the laser alignment assembly has itself been aligned, the cell is replaced. The laser beam should enter the cell and some number of red dots should be seen on the bottom mirror, when viewed through the clear lower window in the otherwise blacked-out glass cylinder. The two external adjustment screws on the top plate can now be adjusted to produce two parallel rows of dots. The pathlength can be calculated with the following formula:

Total pathlength through cell = (number of dots)(1.12 m)

Counting the number of dots can best be done by looking directly down onto the bottom mirror, via the small window in the center of the top plate.

The bottom mirror has two notches that allow the beam to enter and leave the cell. It is important that the row of dots starting from one notch extend to the other notch, so that the beam will pass out of the cell through the exit window when it walks off of the bottom mirror.

See Figure II.F.1.c for examples of aligned and misaligned dot patterns, dot counting tips, and pathlength calculations.

Cell alignment step 4:
Fine alignment of the cell's top mirror/double check of passes

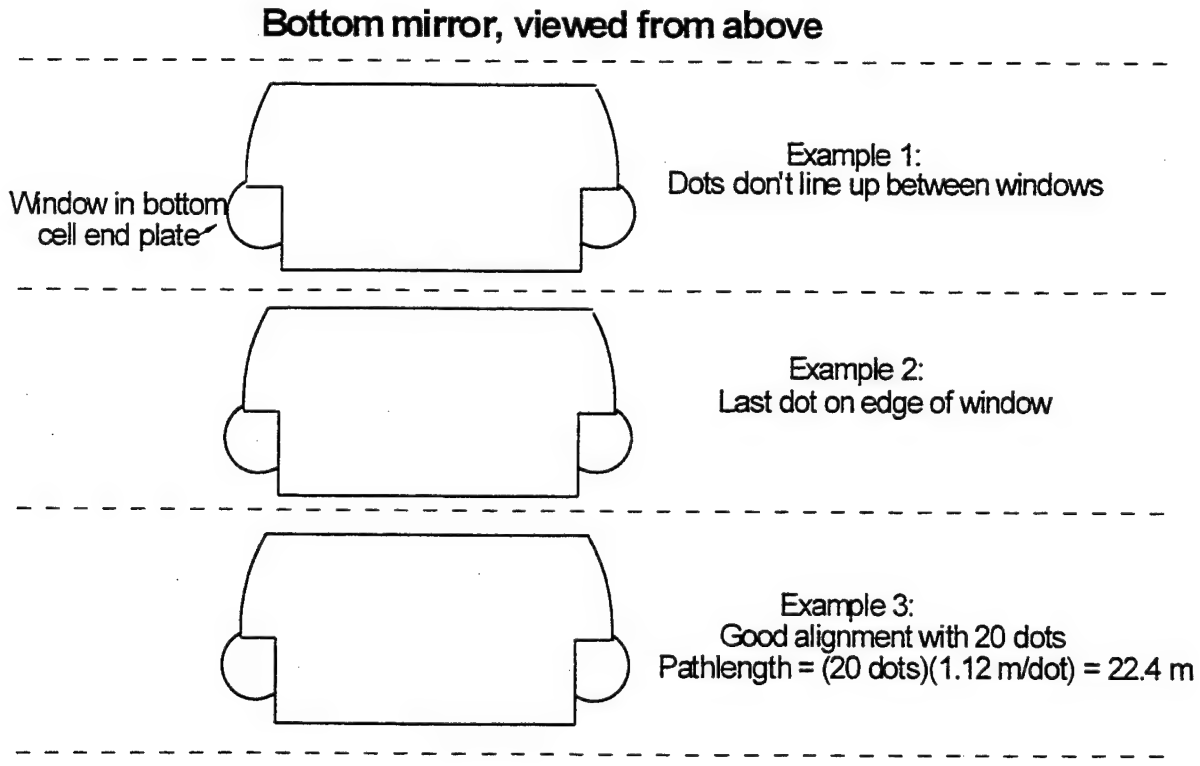


Figure II.F.1.c Examples of good and bad dot patterns and pathlength calculation.

This is the only alignment of the cell that is routinely required. For this alignment step, the infrared energy making it through the cell and onto the FT-IR detector is used as the criterion for maximizing the alignment. Energy on the detector is best determined through the operation of the spectrometer in align mode available in the Grams/32 software environment.

While viewing rapidly collected single-beam spectra in real-time, the external alignment screws on the cell's top end plate are adjusted to optimize the amount of energy seen in the spectra (indicated by the "align percentage" displayed at the bottom left of the align screen).

Very small movements of the external mirror adjustment screws will be required to optimize the alignment. Over-adjusting at this point could result in a maximized alignment position being obtained with a different number of passes than originally set in the previous alignment step. For this reason, the number of laser dots should be counted again after this step to ensure that the number of passes (as indicated by the laser dots) has not changed.

Cell alignment step 5:
Fine alignment of the cell's transfer optics with the cell mounted atop the enclosure

Normally, this step is only necessary after the cell's transfer optics have been grossly adjusted, as described in Cell alignment step 2. Additionally, one may wish to "tweak" the alignment of the transfer optics mirrors after the cell's internal mirrors have been adjusted for maximum energy throughput but this is not necessary for satisfactory performance.

This step must be performed with the cell atop the enclosure. To adjust the alignment screws on the cell's transfer optics box with the cell mounted in this manner, access must be gained to the removable plate in the bottom of the enclosure. For this purpose, two stacks of books may be used to support the ends of the instrument above the bench top.

Similarly to step 4, the mirrors in the cell's transfer optics box are adjusted to optimize the amount of energy while viewing rapidly collected single-beam spectra in real-time. The mirrors are each adjusted with a set of three screws extending out the bottom of the transfer optics box. The middle screw in each set of three must be loosened to allow adjustment. The middle two outside screws in each set of three actually adjust the mirrors' orientations.

Very small movements of the mirror adjustment screws will be required to optimize the alignment at this point. The mirror nearest the detector should be aligned first but an iterative process may be ultimately required to optimize the alignment of both mirrors.

II.F.2 FT-IR alignment

For the most part, the FT-IR components (source assembly, interferometer engine, and detector assembly) are mounted in the enclosure in such a way as to ensure their alignment. Alignment of the FT-IR components therefore is limited to alignment of the interferometer's inner mirrors. The only exception involves the detector assembly, for which there is a small amount of movement possible when its mounting screws are loosened. However, the amount of misalignment possible in this component is not enough to prevent satisfactory operation of the instrument. If desired, "tweaking" of the detector assembly can be performed after all other elements (cell and FT-IR) of the system have been optimally aligned.

Alignment of the Midac interferometer is accomplished via adjustment of the stationary mirror. Two 3/16" socket head alignment screws are provided on the back of the aluminum interferometer block, opposite the infrared source. Long-handled L wrenches provide the greatest sensitivity during the adjustments.

Ultimately, the criterion to be used for characterizing interferometer alignment is the amount of modulation in the interferograms produced, as evidenced by the percentage of ADC filling indicated while the instrument is operated in "align" mode. However, another indicator of alignment is also available and often useful in locating the best alignment. Specifically, the instrument's response at higher wavenumbers is strongly dependent upon interferometer alignment. Even slight misalignment of the interferometer will result in drastic reduction or even elimination of any response beyond about 3000 cm-1. *Viewing of single-beam spectra in real-time using the "Align" mode of Grams/32 is therefore recommended during the alignment procedure.*

When the cell is dismounted from the enclosure (and no other sampling accessories are in it's place), the collimated infrared beam from the interferometer passes directly to the detector. This results in extremely high energy levels on the detector. These high light levels can create anomalies in the data collected, making it difficult or impossible to characterize the instrument's alignment based on the signal being recorded. *It is therefore recommended that the interferometer be aligned after the cell has been aligned and with the cell in place.*

If the interferometer must be aligned without the cell in place, the amount of energy passing to the detector must be reduced. Neutral density filters are designed specifically for this purpose but if none are available, a notecard or similar item can be temporarily inserted between the infrared source assembly and the interferometer to block the beam. The detector will now see the infrared energy emitted by an ambient temperature object, which is low but should be sufficient to allow operation and alignment of the interferometer.

One disadvantage of using the blocked source beam approach to reduce the energy on the detector is that ambient temperature objects emit insufficient high wavenumber energy to result in any signal being displayed by the system beyond approximately 2000 cm-1. High wavenumber throughput is therefore unavailable as an additional alignment criterion.

A warning: The effects of the adjustment screws are interdependent. Aligning the interferometer therefore cannot be accomplished via a step-by-step procedure but rather through the development of a "feel" for the alignment process. Be patient, have faith.

II.G Preparing the hardware for data collection – A step-by-step checklist

1. Fill or top off the detector dewar with liquid nitrogen, as necessary.
2. Install the cell atop the enclosure. Lightly tighten the two 3/16" socket head scres that hold the cell tightly to the enclosure.
3. Connect all lines and sensors to the cell.
4. Boot up the data collection computer and enter the Midac Grams/32 software environment.
5. Connect the cable from the computer to the instrument.
6. Apply power to the instrument.
7. Open the top plate covering the interferometer compartment.
8. Confirm that the instrument is receiving power by noting that interferometer laser is operating.
9. Confirm that the instrument is properly connected to the computer by noting that the mirror drive is scanning slowly back and forth. (The mirror drive will lock and emit a buzz if the instrument is not correctly connected to a computer.)
10. Confirm that the infrared source is glowing orange.
11. In Midac Grams, initiate the "align" mode. Use 4 cm-1 resolution and view single-beam spectra from 0 cm-1 to 8000 cm-1. Set the gain to 1.
12. Confirm that the instrument is operating and in alignment by noting the appearance of the single-beam spectra displayed.
13. Turn on the cell alignment laser.
14. Adjust the pathlength to the desired length by viewing the number of dots on the bottom mirror. View the dots from the window in the cell's top end plate.
15. Perform final alignment of the cell's internal mirrors using the adjustment screws on the cell's top end plate. Use the appearance and intensity of the single-beam spectra displayed while the instrument is in align mode as a criterion for optimizing alignment. Verify that the number of number of dots on the bottom mirror has not changed after making final adjustments.
16. Optimize the pre-amplifier gain if necessary. Alignment percentages between 50% and 95% are satisfactory. Alignment percentages are changed by approximately a factor of two with each consecutive jumper setting.
17. Replace all access cover plates.

III. System software and analytical procedures

III.A Introduction

This section will discuss the software and procedures used for data collection and analysis on the ASI/Demil FT-IR system. The format of this section will be to detail an analytical procedure by demonstrating the software functions required to perform that task. Therefore, the three software packages to be employed with the ASI/Demil FT-IR system will be discussed at various times throughout the section.

The primary software package that will be used in this project is MDGrams/32™ from Galactic Industries. MDGrams/32™ is a spectral data collection and manipulation program that will be used to perform calibration measurements, single sample measurements and continuous data collections. In addition to collecting data, MDGrams/32™ will be used to convert the single-beam spectral data collected into absorbance spectra, perform analysis on absorbance peaks, and analyze sample data using interactive spectral subtraction.

The screen displayed when MDGrams/32™is started is shown in Figure III.A.1. This screen provides a menu driven interface with the FT-IR instrument and spectral data to be collected and manipulated. Besides the normal menus (File, Edit, etc.), MDGrams/32™ also has a button bar that allows for the execution of menu commands with a single mouse action. This button bar is located directly under the menu bar. In addition to the button bar, MDGrams/32™ allows the user to define buttons that execute macros or array basic (Galactics Industries programming language) programs. In Figure III.A.1, the user defined buttons (ABS, SUB, PKS and MFU) are located in the bottom right corner of the screen. This view is actually a view that was created by AeroSurvey, and is stored in the MDGRAMS directory as *asibtns.vw*

The second software package that will be discussed in this section is Midac AutoQuant™. The initial view of Midac AutoQuant™ is shown in Figure III.B.2. Midac AutoQuant™ is a data collection and analysis package that performs continuous monitoring of a process and automated spectral analysis using a classical least squares algorithm. Like MDGrams/32™, Midac AutoQuant™ is a menu driven interface between the user, the instrument and the spectral data. For the purposes of this manual, Midac AutoQuant™ will be used only to perform the analysis of continuous monitoring data using the batch analysis function.

The final software package that will be discussed throughout this section is Microsoft® Excel'97. Microsoft® Excel'97 is a powerful spreadsheet program that will be used for the plotting and evaluation of calibration data and data analysis results obtained from Midac AutoQuant™.

Figure III.A.1. Initial screen display of MDGrams/32™

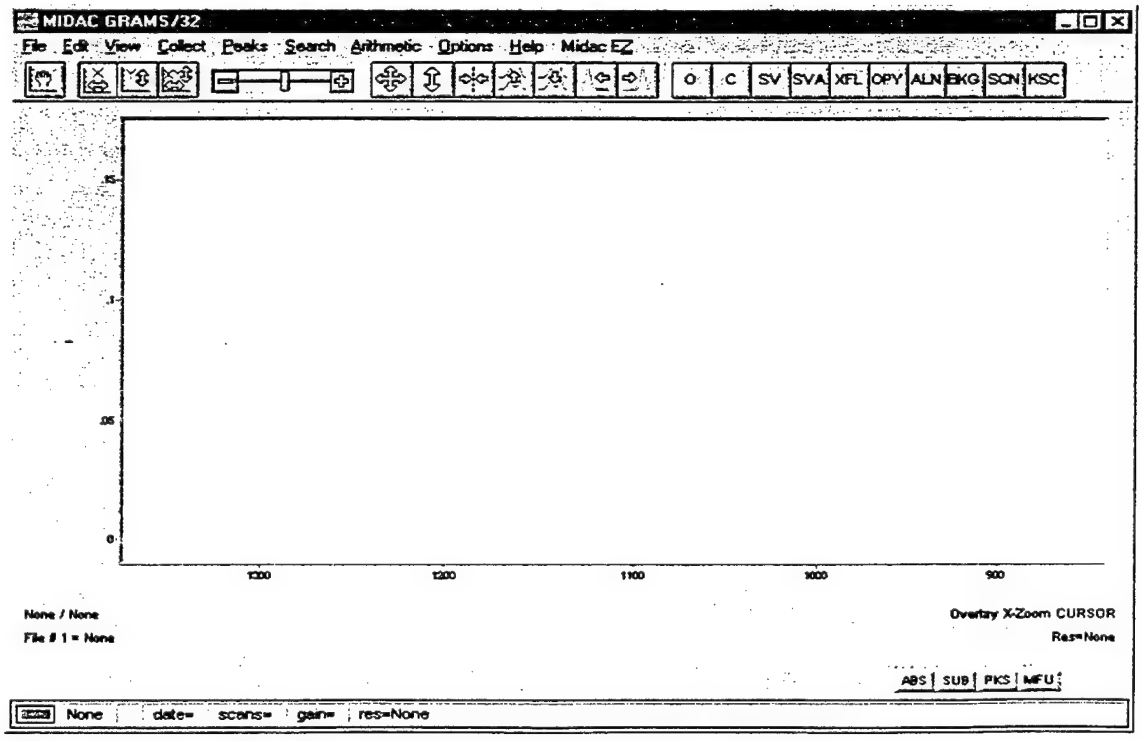
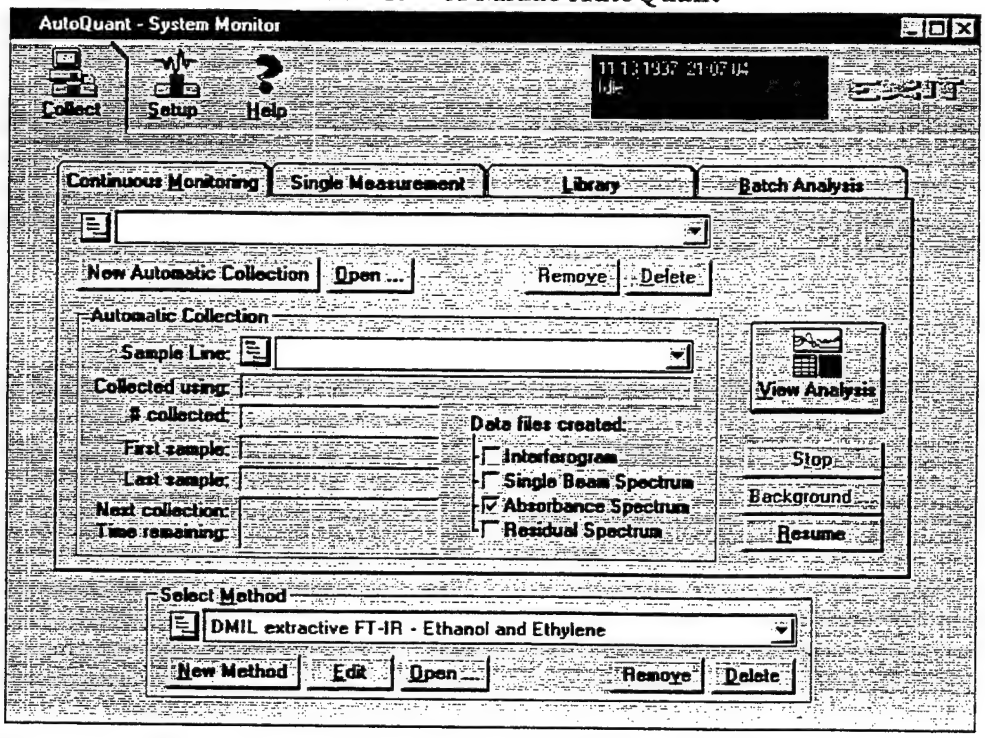


Figure III.A.2 The initial view of Midac AutoQuant™



III.B. Creating a set of calibration spectra

In general, the instrumentation should be allowed to run for a minimum of 3 hours before any meaningful spectra are collected. This warm-up period allows the interferometer block and associated electronics to reach a stable temperature. By allowing the instrument to reach a stable temperature, the system noise is drastically reduced and chances of encountering instrumentation "glitches" or drift are minimized.

The process of creating a set of calibration spectra is probably the most crucial part of collecting quantitative FT-IR data. If the calibration spectrum used in quantitative analysis is incorrect, all quantitative numbers derived from that calibration spectrum will also be incorrect. In theory, a set of calibration spectra could consist of a single absorbance spectrum of the analyte collected at a known concentration. However, single-point calibrations are risky at best, and it is recommended that a minimum of four different samples spanning an order of magnitude in concentration be used to create a set of calibration spectra. This minimum requirement will establish a statistical basis for subsequent measurements and allow the linearity range of the instrumentation to be verified.

For this project, all calibration spectra and the corresponding QA/QC data will be collected with MDGrams/32™ and the resulting data will be plotted in Microsoft® Excel'97. When MDGrams/32™ and Microsoft® Excel'97 are used in conjunction, it is possible to generate a set of high quality calibration spectra and a corresponding Beer's law plot that will give the end user a high degree of confidence in any subsequent measurements.

III.B.1 MDGrams/32™

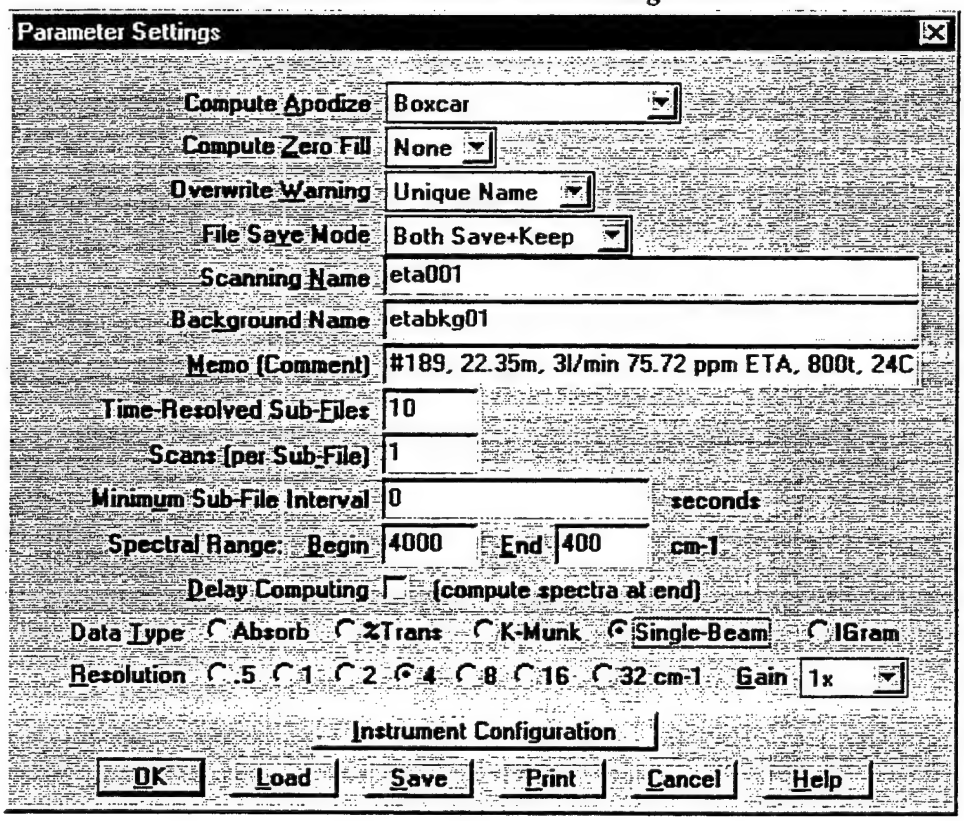
a) Setting instrument parameters.

As explained in Section I.C.3, the exact data collection parameters used in a particular experiment should be determined by the chemistry of the process being studied and the overall goals of that experiment. Once the parameters for a given experiment are determined, calibration data should be collected using the same parameters. *It cannot be stressed enough that the best possible data analysis results will be obtained when the calibration data used to analyze a sample spectrum are collected on the same instrumentation and under the same instrument parameters as the sample spectrum.*

Once the parameters for an experiment are determined, the process of setting those parameters in MDGrams/32™ is straightforward. Figure III.B.1 shows the *Parameter Settings* menu (|Collect|Parameter Settings) within MDGrams/32™. As can be seen in Figure III.B.1, this menu includes not only instrument parameters, but also some file options as well.

From this menu the apodization function, FFT zero filling, number of coadded scans, spectral range, data type, resolution, and gain can be set. Once these parameters are set,

Figure III.B.1. MDGrams/32™ *Parameter Settings* menu



the values will remain as defaults until they are changed. As will be seen later, all of these parameters, excluding apodization function and FFT zero-filling, can also be changed within menus presented at the initiation of data collection scanning.

The *Instrument Configuration* button on this menu leads to a menu that allows the changing of fundamental instrument settings such as the laser wavelength. It should not be necessary to change these settings on the ASI/Demil FT-IR, and, therefore, these options will not be discussed.

b) Alignment of the instrument and gas cell.

The alignment of the instrument and gas cell can be checked using the alignment menu that is shown in Figure III.B.2. This menu can be accessed using the ALN button on the MDGrams/32™ main view, or from the Collect menu. The menu allows you to set the spectral range to view, data type to view, the resolution to use while scanning in align mode, and the gain to use during alignment. It is generally best to view align mode at 4 cm-1 resolution or lower so that any changes that may be made to the alignment are reflected immediately by a change in energy on the detector. It is also useful to check the alignment while viewing a single beam spectrum, displayed from 0 cm^{-1} to 8000 cm^{-1}. This allows the detector response envelope to be checked for any deviations from the norm.

Figure II.B.3 shows the MDGrams/32™ alignment screen. From this screen, the detector envelope and the relative amount of energy on the detector can be monitored. The amount of energy incident upon the detector is shown as a percentage of the capacity of the analog-to-digital converter (ADC). This number should be maximized whenever collecting data. It is preferable to have at least 50% for the collection of spectra; ADC filling percentages in the 80%-90% region are optimal.

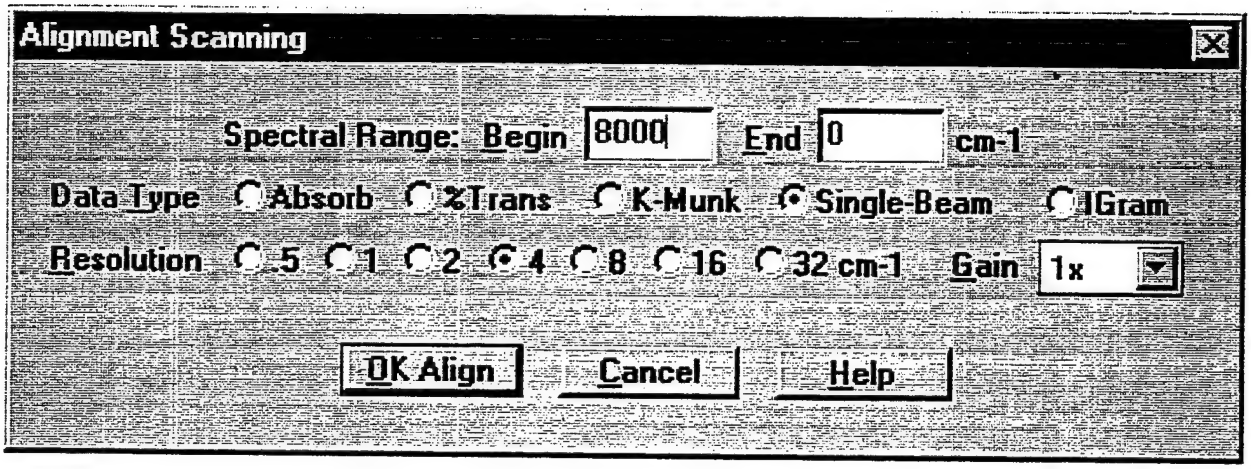
All of the instrument and gas cell components are hard mounted into place within the enclosure of the ASI/Demil FT-IR system and the optical alignment of the system should not change in routine use. Mis-alignment is evidenced by low energy on the detector and, possibly, noticeable differences in the appearance of the single-beam spectra collected. Section II of this manual details steps for aligning the gas cell and FT-IR system.

c) Setting the flow parameters and purging the gas cell.

The ASI/Demil FT-IR system is equipped with an Alicat PVU-10SLPM-S flow/pressure/temperature sensor at the input of the gas cell. This sensor will be the basis for setting the flow parameters.

The following procedure should be accomplished

Figure II.B.2 The MDGrams/32™ *Alignment* menu.



using nitrogen gas only until the flow system is set at a known and controllable pressure and flow rate.

Initially, the valve on the exit of the gas cell and the valve on the gas delivery regulator should be closed. The regulator on the nitrogen cylinder should be set to deliver a pressure of approximately 15 psig.

First, set the display on the Alicat sensor to show the flow rate in liters/minute. Next, completely open the valve on the exit of the gas cell. Then, slowly, open the exit valve on the gas regulator until the Alicat sensor shows a flow rate of 3 liters/minute. When the flow rate has been achieved, switch the Alicat sensor to display the pressure in torr. Slowly begin to close the valve on the exit of the gas cell while monitoring the pressure on the Alicat sensor. Quit turning the exit valve when the pressure in the system has reached 800 torr. Now switch the Alicat sensor to display flow rate again. If the flow rate has changed drastically, it may be necessary to iterate the valve adjustment process until the desired flow rate and pressure can be achieved.

Once the desired flow rate and pressure have been established, note the delivery pressure on the nitrogen regulator. If the valves are not adjusted, this delivery pressure should get the system close to 3 liters/minute and 800 torr with most gases that will be flowed through the system. Once a new gas is flowing in the system, the valves can be adjusted to fine tune the systems flow rate and pressure. This procedure can be followed to achieve any desired set of flow parameters. The values of 3 liters/minute flow rate and 800 torr system pressure are common parameter settings used in extractive FT-IR. Different experiments may require different parameters.

An experiment was performed to determine the amount of time that the gases should be flowed through the cell in order to achieve a satisfactorily complete turn-over of the cell contents. The details of this experiment are presented in Appendix D of this manual.

d) Collecting a background single beam spectrum.

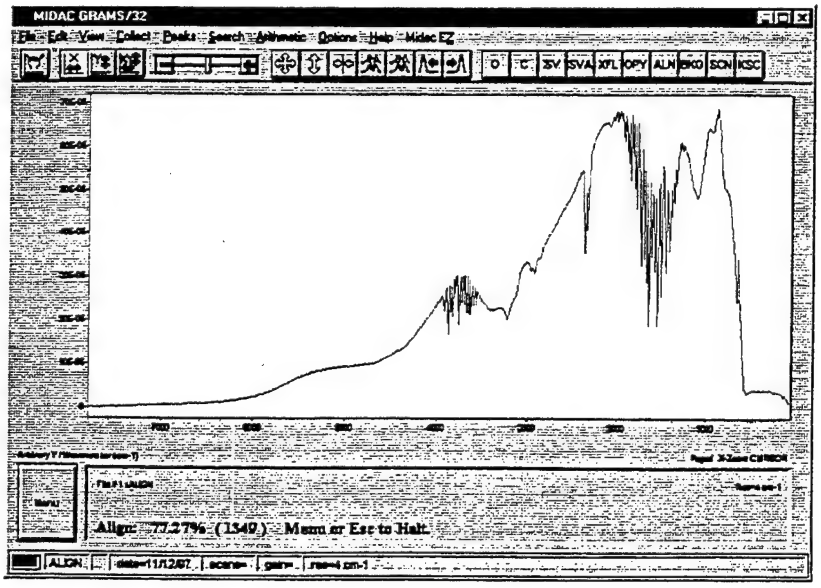
While it is possible to collect calibration spectra as absorbance files directly, AeroSurvey recommends collecting calibration data as single beam spectra and subsequently converting the single-beam spectra to absorbance spectra within MDGrams/32™. Background and sample single-beam spectra can therefore both be collected using the *Normal Scanning* menu. By collecting and saving single-beam spectra, the flexibility exists to change the single- beam spectrum used for the background spectrum if any problems are discovered during or after the calibration procedure.

The *Normal Scanning* menu can be accessed using the SCN button on the main view of MDGrams/32™, or can be accessed through the Collect menu on the menu bar of MDGrams/32™.

Figure II.B.4 shows the scanning menu. This menu has file options that allow the assignment of a filename, an appropriate memo that will be placed in the file header, and the data type to be collected. It also gives the option to change the number of coadded scans to be collected, the instrument resolution, the spectral range to be used, and the instrument gain setting.

When scanning is started, the normal scanning view is displayed. This view is shown in Figure II.B.5. As can be seen in the figure, the view displays the single beam spectrum being collected and the number of scans that are being coadded. When the collection of this file is completed, the file will both be saved to disk according to the path set in the *Normal Scanning* menu and kept open in memory as the active spectrum file in MDGrams/32™.

Figure II.B.3 The MDGrams/32™ alignment screen



e) Collecting QA/QC data.

The QA/QC data described here is similar to what is termed the *calibration transfer standard* in the EPA protocol on extractive FT-IR for monitoring gaseous emissions from a stationary source (see Appendix B). The purpose of collecting this data is to ensure that the instrument response at the time the sample spectra are collected is consistent with the response when the calibration spectra are collected.

The actual sample that is used to collect this data should be a compound that has absorbance features in the same region of the spectrum as the sample analytes. The QA/QC sample should be obtained as a certified reference gas mixture in nitrogen that is traceable to accepted laboratory methods. The QA/QC sample spectra should be collected under the same conditions as the calibration sample spectrum and the analyte sample spectrum. A common compound that is used as a QA/QC sample is ethylene.

Ideally, a four point calibration curve would be generated for the QA/QC sample analyte, and the actual sample used to collect the QA/QC data would be a representative sample of that calibration.

This, however, is not always necessary. The purpose of the QA/QC sample is to provide a consistent basis for comparison from one time of instrument use to another. Therefore, as long as the sample is consistent from one time to another, any trends that may be observed in the QA/QC data will be valid.

The QA/QC data collected during instrument calibration should be treated as another calibration sample. All of the instrument and gas flow parameters should be the same as those used to collect the calibration background spectrum and the calibration sample spectra.

The QA/QC spectrum is collected from the *Normal Scanning* menu shown in Figure III.B.4 and the single beam spectrum should be similar (having the addition of the sample absorbance bands) to the single beam observed during the background spectrum collection shown in Figure III.B.5.

Once this spectrum is collected, an absorbance spectrum should be created and archived for use as a QA/QC reference spectrum during monitoring applications

f) Collecting a sample spectrum.

Collection of the sample calibration spectrum is performed from the *Normal Scanning* menu as seen in Figure III.B.4. The major consideration in collecting the calibration sample spectrum is that all conditions (instrument and flow parameters) are identical to those used to collect the calibration background spectrum. The only difference between the two samples should be the analyte. Again, while this sample is being collected, the normal scanning view will be displayed as shown in Figure III.B.5.

g) Creating an absorbance spectrum.

Once the calibration background single beam spectrum and the calibration sample single beam spectrum

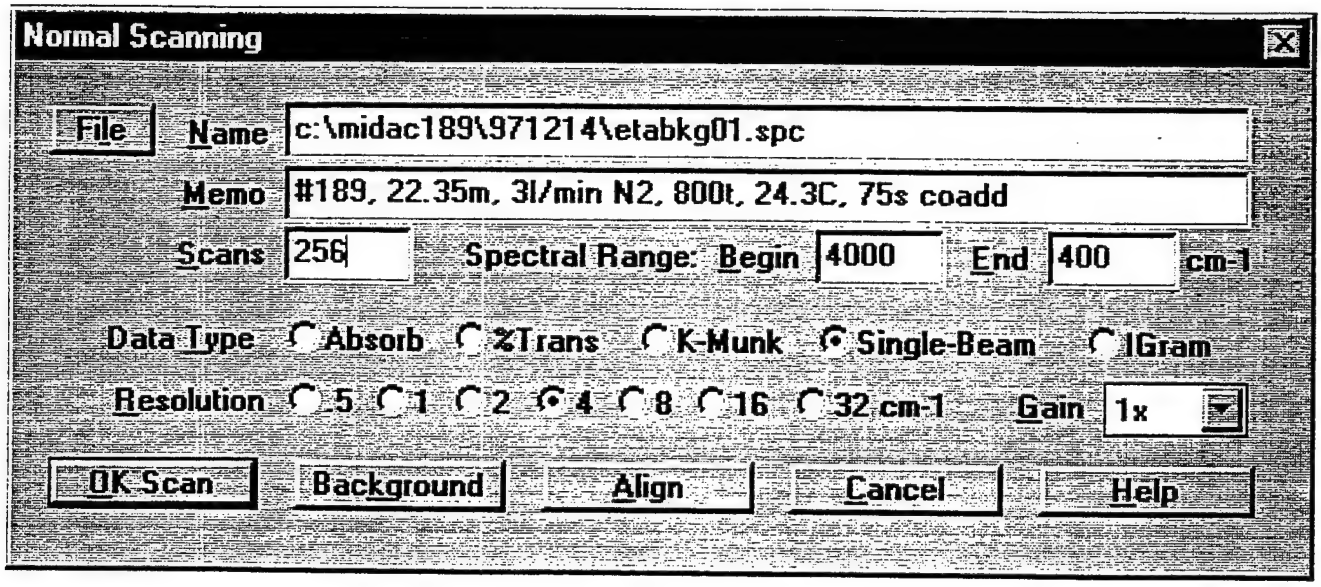


Figure II.B.4 The *Normal Scanning* menu in MDGrams/32™.

Figure II.B.5. The normal scanning view in MDGrams/32™

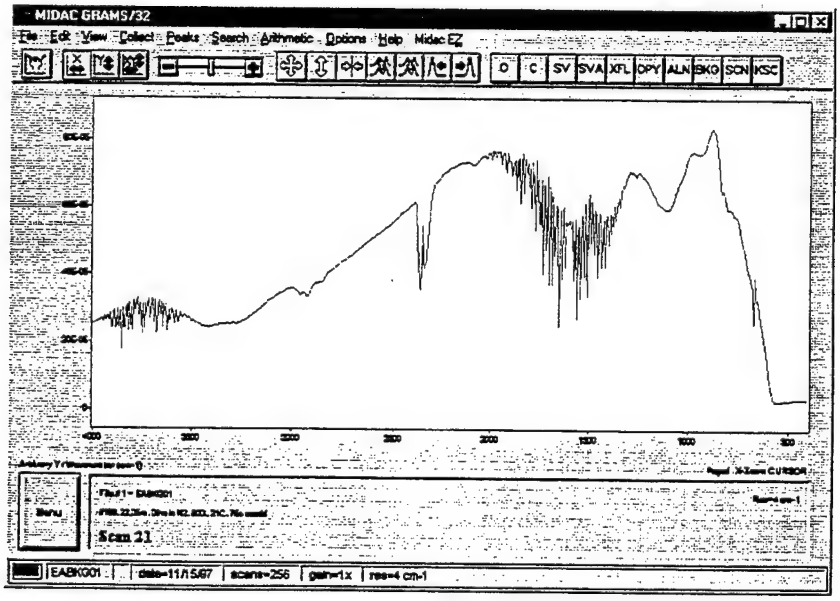


Figure III.B.6 The *Background Selection Menu* from *abs.ab*

have been collected, an absorbance spectrum should be created. The creation of an absorbance spectrum is accomplished using the array basic routine *abs.ab*. This routine is accessed from the main-view by the user assigned button ABS in the lower right corner of the view.

The initial interface is the *Background Selection Menu* that is shown in Figure III.B.6. This menu lists the files that are open in the computer's memory. The current sample spectrum is denoted with a #S and the current background spectrum, if open in memory, will be denoted with a #R.

If the background spectrum that is going to be used in the creation of the absorbance spectrum is not listed as #R, but is listed as open in memory, all that needs to be done is to double click on the background spectrum name and the *abs.ab* will execute. It he background spectrum that is being used is

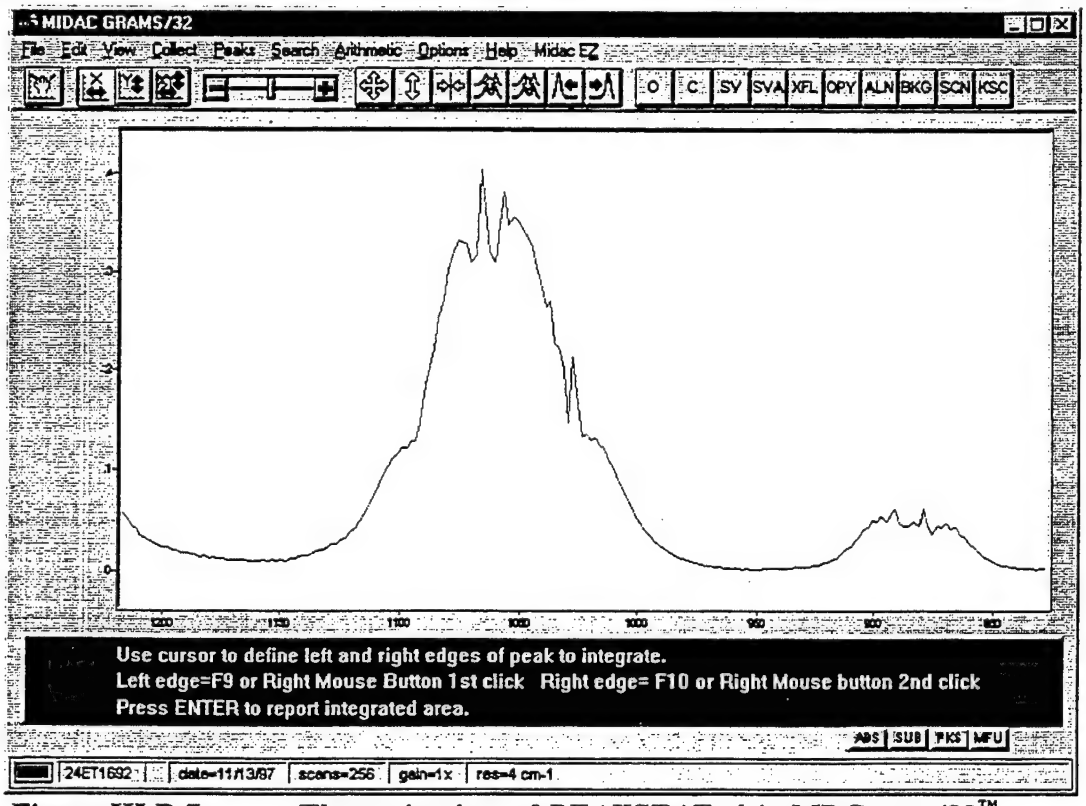
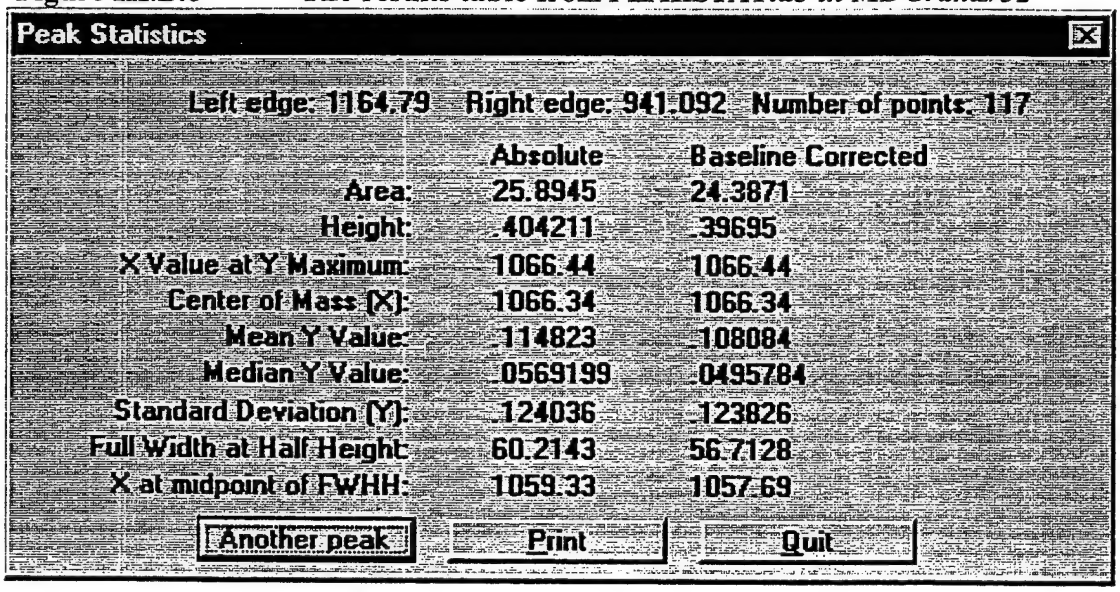


Figure III.B.7 The main view of *PEAKSTAT.ab* in MDGrams/32™.

Figure III.B.8 The results table from *PEAKSTAT.ab in MDGrams/32™*



not listed as open in memory, double click on the *Open Disk File* choice and the *Select #R* menu will appear. From this menu, select the appropriate computer path and filename for the background spectrum to be used. Double click on the filename and *abs.ab* will then execute automatically.

h) Creating a Beer's Law plot.

After all of the calibration samples are converted to absorbance files, the absorbance spectra should be analyzed for peak absorbance and peak area values. The absorbance peak to be used in the analysis must first be chosen. Unless there are special considerations due to the particular process being monitored, the most intense band is generally chosen to perform quantitative analysis for an analyte.

Once this band is determined, the MDGrams/32™ view can be expanded to show only the absorbance band of interest. After the proper view is established, hit the PKS button at the bottom right of the main view in MDGrams/32™ to execute *PEAKSTAT*.ab. The peakstat view that appears is shown in Figure III.B.7. The baseline is drawn using the cursor to click at the appropriate wavenumber at the left and right of the absorbance band. After the baseline is drawn, hit return. A table of results from *PEAKSTAT*.ab like that in Figure III.B.8 is shown. This table gives the peak height and peak area values that should be used to create the Beer's law plot. The values that should be used for this purpose are the Baseline Corrected values.

Once the values for the peak absorbance are obtained for all of the calibration samples, these values can be plugged into Microsoft® Excel '97 to create an actual Beer's law plot for the calibration.

To facilitate this, spreadsheet files have been included with the ASI/Demil FT-IR system. These files can be found in the Midac189\calib directory (ethylene.xls and ethanol.xls). There are three main portions to these spreadsheets. The first two parts are file and absorbance band information like that shown in Figure III.B.9. The third portion of the spreadsheet is the results of a linear regression analysis. This portion of the spreadsheet is shown in Figure III.B.10. Once the appropriate file information and collection conditions are entered, only the peak absorbance and peak area values need to be entered, the corrected values and the absorptivites are calculated automatically by the spreadsheet. Once this task is accomplished, the regression analysis should be performed. The regression analysis is performed from the |Tools|Data Analysis menu. The regression analysis menu is shown in Figure III.B.11.

The Input-Y range is the corrected peak absorbance value in the spreadsheet. The corrected value is used for all analytes so that a direct comparison of absorptivities can be made without the regard to the sample conditions. The X-Input values are the column densities of each calibration sample. The Summary Output should be placed over the top of the existing Summary, and the Residuals should be calculated so that the regression line can be plotted with the actual sample absorbance values. If peak area is used instead of peak height, simply input the corrected peak area for the Y-input value instead of the corrected peak absorbance, and the remaining steps are the same.

After completion of the regression analysis, the Beer's law plot can be made. Figure III.B.12 show an example of such a plot.

Ethanol, 1066.4 cm-1, 200 C											
Compound	Ethanol	Calculation of Absorptivity									
Peak Frequency (cm-1)	1066.4										
Cell Temperature (C)	200										
Filenames	ehs*.*	Filename	Date	Sample Temperature (C)	Sample Pressure (torr)	peak absorbance	corrected absorbance (760 torr, 25C)	reference gas concentration (ppm)	reference gas column density (ppm*m)	absorptivity (ppm*m)-1	corrected absorptivity (ppm*m)-1
Background File	ehb*.*										
Computer and Directory	433/l c:\erdec\971012	ehs200a	12-Oct-97	182	800	0.0388	0.0563	1251.3	250.26	1.55E-04	2.25E-04
Instrument #	135	ehs200b	12-Oct-97	183	800	0.0764	0.1110	2506.9	501.38	1.52E-04	2.21E-04
Collection Mode	Monostatic	ehs200c	12-Oct-97	183	800	0.1513	0.2199	5003.6	1000.72	1.51E-04	2.20E-04
# of scans	64	ehs200d	12-Oct-97	183	800	0.2419	0.3516	8015.2	1603.04	1.51E-04	2.19E-04
Resolution (cm-1)	4	ehs200e	12-Oct-97	183	800	0.2379	0.3458	7994.2	1598.84	1.49E-04	2.16E-04
Integration time (seconds)	9										
Detector	MCT										
Source	Internal SiC										
Beamsplitter	ZnSe										
Gas Cell	10 cm heated										
Optical Pathlength (meters)	0.2										

Figure III.B.9 **The file and spectral information from the Microsoft® Excel '97Spreadsheet.**

Figure III.B.10 The regression analysis output from Microsoft® Excel '97

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.99986							
R Square	0.99971							
Adjusted R Square	0.74971							
Standard Error	0.00227							
Observations	5							
ANOVA								
	df	*SS*	*MS*	*F*	*Significance F*			
Regression	1	0.07174	0.07174	13932.20	1.341E-06			
Residual	4	0.00002	0.00001					
Total	5	0.07177						
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	2.183E-04	8.941E-07	244.16750	1.688E-09	2.158E-04	2.208E-04	2.158E-04	2.208E-04
RESIDUAL OUTPUT								
Observation	*Predicted Y*	*Residuals*						
1	0.05464	0.00163						
2	0.10946	0.00158						
3	0.21847	0.00143						
4	0.34997	0.00162						
5	0.34905	-0.00328						

Figure III.B.11 The Regression Analysis Menu from Microsoft® Excel '97.

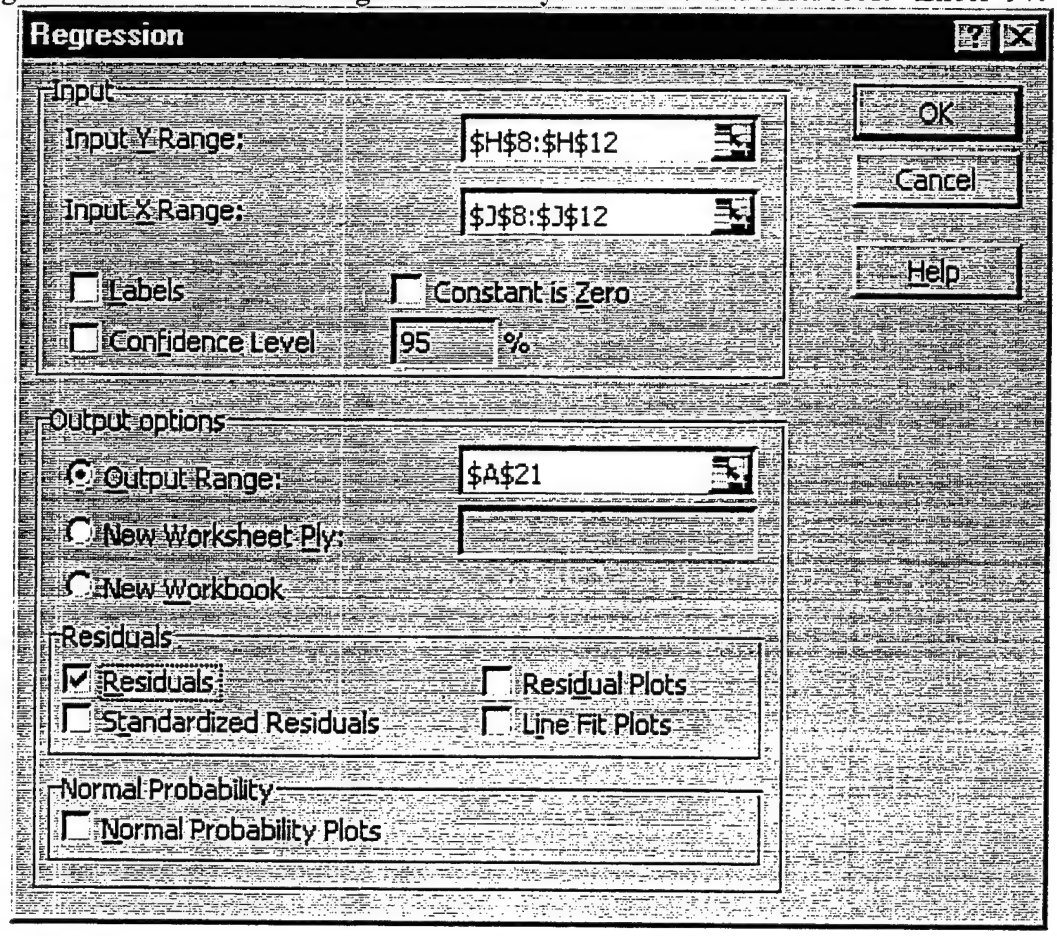
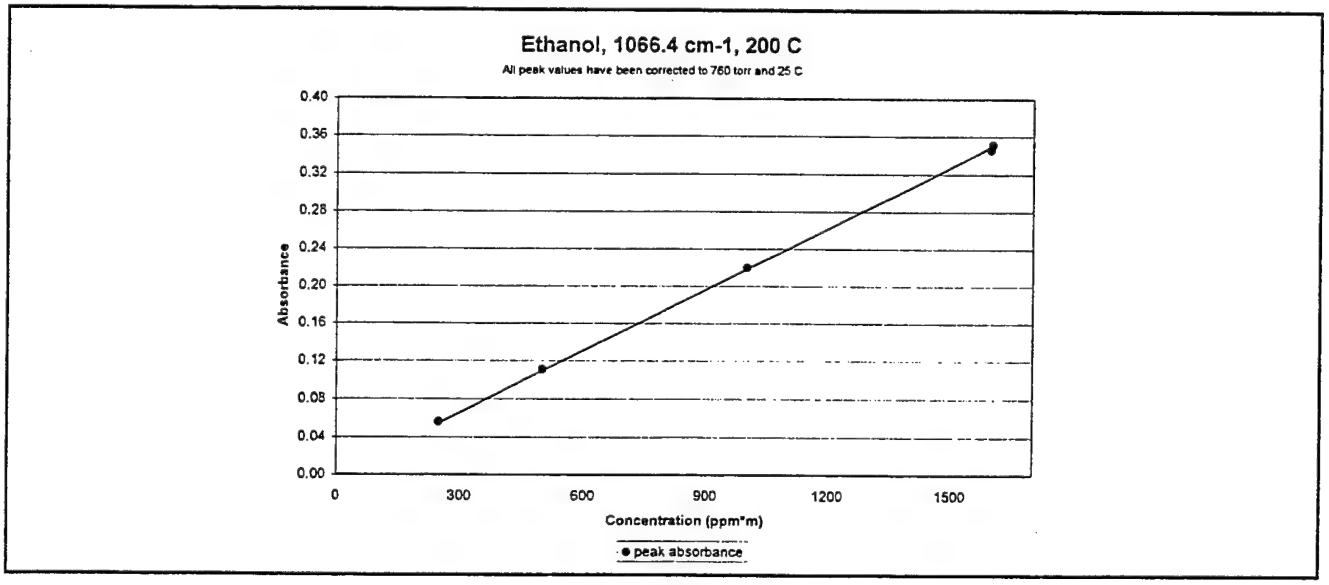


Figure III.B.12 An example of a Beer's law plot from Microsoft® Excel '97.



III.C Performing an Individual Sample Measurement

In many instances, only a single measurement of a sample or process may be required to obtain the desired information. In this instance, a single sample spectrum can be collected much like the calibration spectrum would be collected. (In fact, much of this section is taken directly from Section III.B. For readers who do not wish to repeat the discussions found in Section III.B, sections III.C.1.a through III.C.1.d can be ignored, Sections III.C.1.e through III.C.1.g have been slightly modified and should be reviewed. Sections III.C.1.h and III.C.1.i, however, are new discussions concerning data analysis and evaluation and should be given careful consideration.)

III.C.1 MDGrams/32™

a) a) Setting instrument parameters.

As mentioned in the previous section on the collection of calibration data, consideration of the process being monitored should drive all decisions concerning data collection parameters *and then the same parameters should be used for the collection of calibration and sample spectra.* Setting parameters for the sample spectra is done in the same fashion as was used to set the parameters for the calibration data collection. Figure III.B.1 shows the *Parameter Settings* menu (|Collect|Parameter Settings) within MDGrams/32™. As can be seen in Figure III.B.1, this menu includes not only instrument parameters, but also some file options as well.

From this menu the apodization function, FFT zero filling, number of coadded scans, spectral range, data type, resolution, and gain can be set. Once these parameters are set, the values will remain as defaults until they are changed. As will be seen later, all of these parameters, excluding apodization function and FFT zero-filling, can also be changed within menus presented at the initiation of data collection scanning.

The *Instrument Configuration* button on this menu leads to a menu that allows the changing of fundamental instrument settings such as the laser wavelength. It should not be necessary to change these settings on the ASI/Demil FT-IR, and, therefore, these options will not be discussed.

b) Alignment of the instrument and gas cell.

The alignment of the instrument and gas cell can be checked using the alignment menu that is shown in Figure III.B.2. This menu can be accessed using the ALN button on the MDGrams/32™ main view, or from the Collect menu. The menu allows you to set the spectral range to view, data type to view, the resolution to use while scanning in align mode, and the gain to use during alignment. It is generally best to view align mode at 4 cm-1 resolution or lower so that any changes that may be made to the alignment are reflected immediately by a change in energy on the detector. It is also useful to check the alignment while viewing a single beam spectrum, displayed from 0 cm^{-1} to 8000 cm^{-1}. This allows the detector response envelope to be checked for any deviations from the norm.

Figure II.B.3 shows the MDGrams/32™ alignment screen. From this screen, the detector envelope and the relative amount of energy on the detector can be monitored. The amount of energy incident upon the detector is shown as a percentage of the capacity of the analog-to-digital converter (ADC). This number should be maximized whenever collecting data. It is preferable to have at least 50% for the collection of spectra; ADC filling percentages in the 80%-90% region are optimal.

All of the instrument and gas cell components are hard mounted into place within the enclosure of the ASI/Demil FT-IR system and the optical alignment of the system should not change in routine use. Mis-alignment is evidenced by low energy on the detector and, possibly, noticeable differences in the appearance of the single-beam spectra collected. Section II of this manual details steps for aligning the gas cell and FT-IR system.

c) Setting the flow parameters and purging the gas cell.

The ASI/Demil FT-IR system is equipped with an Alicat PVU-10SLPM-S flow/pressure/temperature sensor at the input of the gas cell. This sensor will be the basis for setting the flow parameters.

The following procedure should be accomplished using nitrogen gas only until the flow system is set at a known and controllable pressure and flow rate.

Initially, the valve on the exit of the gas cell and the valve on the gas delivery regulator should be closed. The regulator on the nitrogen cylinder should be set to deliver a pressure of approximately 15 psig.

First, set the display on the Alicat sensor to show the flow rate in liters/minute. Next, completely open the valve on the exit of the gas cell. Then, slowly, open the exit valve on the gas regulator until the Alicat sensor shows a flow rate of 3 liters/minute. When the flow rate has been achieved, switch the Alicat sensor to display the pressure in torr. Slowly begin to close the valve on the exit of the gas cell while monitoring the pressure on the Alicat sensor. Quit turning the exit valve when the pressure in the system has reached 800 torr. Now switch the Alicat sensor to display flow rate again. If the flow rate has changed drastically, it may be necessary to iterate the valve

adjustment process until the desired flow rate and pressurecan be achieved.

Once the desired flow rate and pressure have been established, note the delivery pressure on the nitrogen regulator. If the valves are not adjusted, this delivery pressure should get the system close to 3 liters/minute and 800 torr with most gases that will be flowed through the system. Once a new gas is flowing in the system, the valves can be adjusted to fine tune the systems flow rate and pressure. This procedure can be followed to achieve any desired set of flow parameters. The values of 3 liters/minute flow rate and 800 torr system pressure are common parameter settings used in extractive FT-IR. Different experiments may require different parameters.

An experiment was performed to determine the amount of time that the gases should be flowed through the cell in order to achieve a satisfactorily complete turn-over of the cell contents. The details of this experiment are presented in Appendix D of this manual.

d) Collecting a background single beam spectrum.

While it is possible to collect sample spectra as absorbance files directly, AeroSurvey recommends collecting sample data as single beam spectra and subsequently converting the single-beam spectra to absorbance spectra within MDGrams/32™. Background and sample single-beam spectra can therefore both be collected using the *Normal Scanning* menu. By collecting and saving single-beam spectra, the flexibility exists to change the single-beam spectrum used for the background spectrum if any problems are discovered during or after the calibration procedure.

The *Normal Scanning* menu can be accessed using the SCN button on the main view of MDGrams/32™, or can be accessed through the Collect menu on the menu bar of MDGrams/32™.

Figure II.B.4 shows the scanning menu. This menu has file options that allow the assignment of a filename, an appropriate memo that will be placed in the file header, and the data type to be collected. It also gives the option to change the number of coadded scans to be collected, the instrument resolution, the spectral range to be used, and the instrument gain setting.

When scanning is started, the normal scanning view is displayed. This view is shown in Figure II.B.5. As can be seen in the figure, the view displays the single beam spectrum being collected and the number of scans that are being coadded. When the collection of this file is completed, the file will both be saved to disk according to the path set in the *Normal Scanning* menu and kept open in memory as the active spectrum file in MDGrams/32™.

e) Collecting QA/QC data.

The QA/QC data described here is similar to what is termed the calibration transfer standard in the EPA protocol on extractive FT-IR for monitoring gaseous emissions from a stationary source (see Appendix B). The purpose of collecting this data is to ensure that the instrument response has not changed since the calibration spectra were collected.

Samples of the QA/QC certified reference gas should be flowed through the sampling system and subsequently analyzed just as any other analyte, using the QA/QC reference spectrum collected during the calibration procedure as the basis for quantitative analysis.

f) Collecting a sample spectrum.

Collection of an individual sample spectrum is performed from the *Normal Scanning* menu as seen in Figure III.B.4. The major consideration in collecting an individual sample spectrum is that all conditions (instrument and flow parameters) are identical to those used to collect the relevant background spectrum and the calibration spectra to be used in the data analysis.

g) Creating an absorbance spectrum.

Once the relevant background single beam spectra and the individual sample single beam spectra have been collected, absorbance spectra should be created. The creation of absorbance spectra is accomplished using the Array Basic routine *abs.ab*. This routine is accessed from the main-view by the user assigned button ABS in the lower right corner of the view.

The initial interface is the *Background Selection Menu* that is shown in Figure III.B.6. This menu lists the files that are open in the computers memory. The current sample spectrum is denoted with a #S and the current background spectrum, if open in memory, will be denoted with a #R.

If the relevant background single beam spectrum to be used in the creation of the sample absorbance spectrum is not listed as #R, but is listed as open in memory, all that needs to be done is to double click on the background spectrum name and the *abs.ab* will execute. It he background spectrum that is being used is not listed as open in memory, double click on the *Open Disk File* choice and the *Select #R* menu will appear. From this menu, select the appropriate computer path and filename for the background spectrum to be used. Double click on the filename and *abs.ab* will execute automatically.

h) Analyzing the sample spectrum with spectral subtraction.

An individual sample measurement can be analyzed using spectral subtraction in MDGrams/32™. The general principles of spectral subtraction are outlined in Section I.D. The specific procedures used for the spectral subtraction in MDGrams/32™ are outlined here.

Once the sample absorbance spectrum has been created and is active in the MDGrams/32™ main view, the spectral subtraction routine is accessed using either the |Arithmetic|Subtraction menu commands, or by clicking on the user defined button SUB. Both of these methods access an Array Basic routine called *subtraction.ab*. The main view of *subtraction.ab* is shown in Figure III.C.1. The bottom portion of this view shows an overlay of the sample and calibration (subtrahend) spectrum. The top spectrum shown in this view is the resulting spectrum when the subtraction is applied according to the subtraction options. In this case, the result is showing negative absorbance peaks because the initial default coefficient of unity is too high and ethanol has been over-subtracted from the sample. As illustrated in Figure III.C.2, this spectrum should show the analyte absorbance band stripped out of the sample spectrum when the subtraction is complete. A realistic spectral subtraction result is shown in Figure I.D.

The subtraction options can be set on the left side of this view. The default value for the subtraction coefficient is 1. This value can be changed by typing a value in the box, or by toggling the +/- keys. The increment of change that is seen when using the +/- keys is show under the actual coefficient.

When the analyte absorbance band has been stripped from the sample spectrum, either another sample component can be subtracted by choosing another subtrahend spectrum, or the routine can be exited. Upon exit of the routine, the result can be discarded, or it can be saved to memory under either the old filename or as a new file. It is recommended that a new filename be given to the result if this spectrum is to be kept.

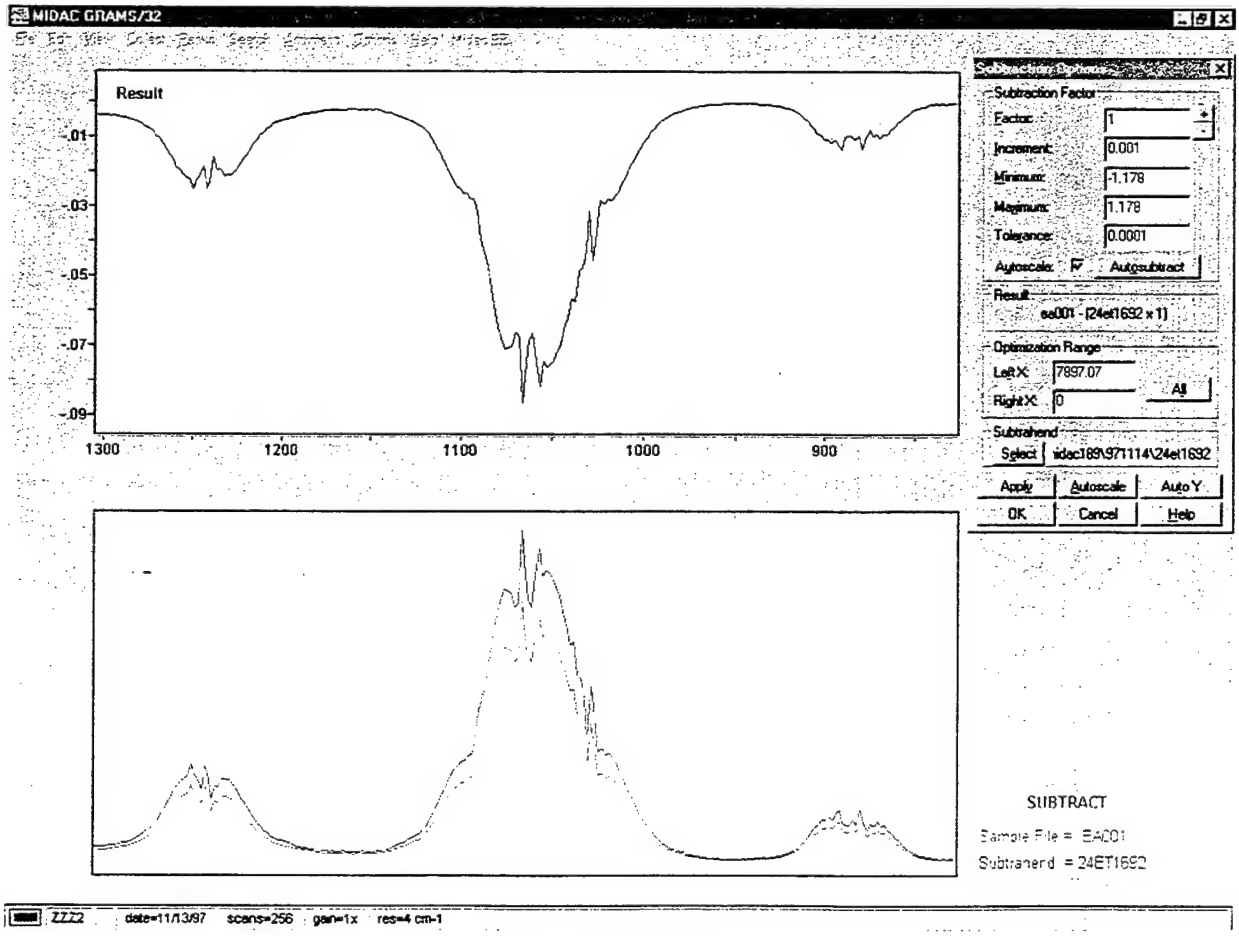
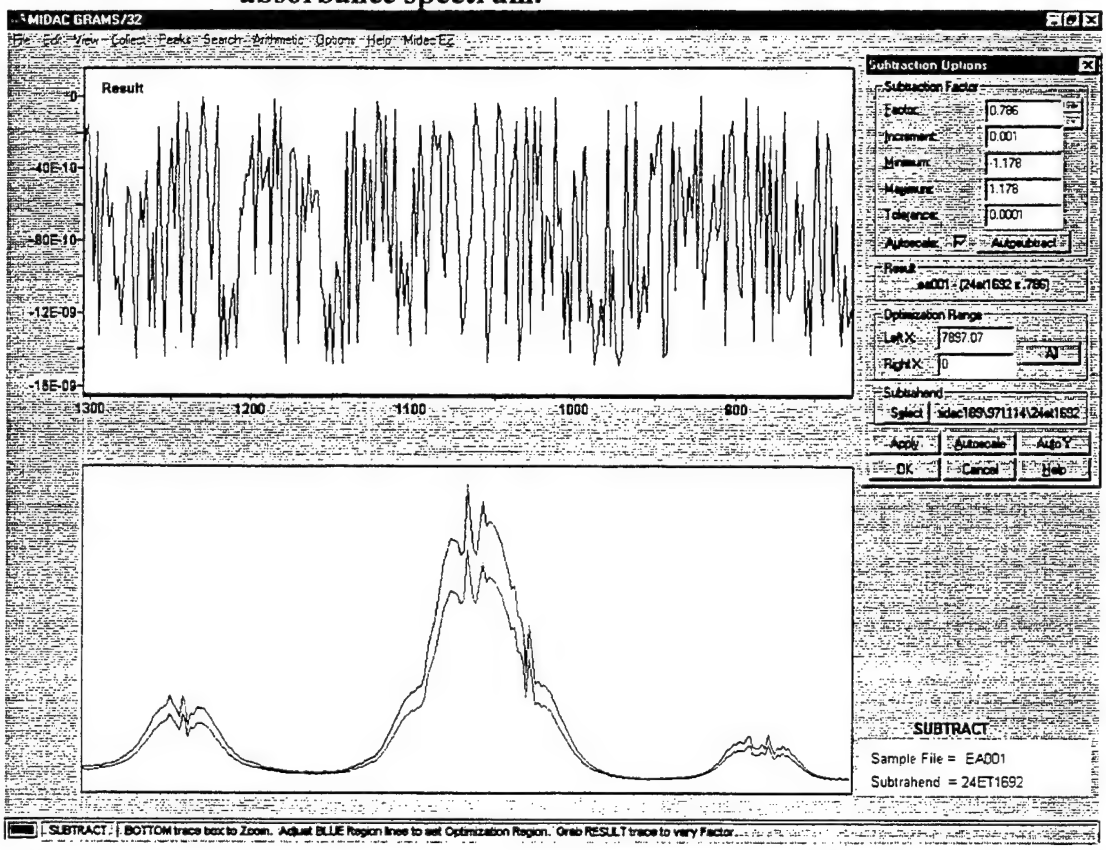


Figure III.C.1 The main view of *subtraction.ab*.

Figure III.C.2 The result of subtracting the proper amount of ethanol from the sample absorbance spectrum.



III.D Performing a Continuous Collection

III.D.1 MDGrams/32™

For the purposes of monitoring a process or event over time, it is convenient to set up a routine that automatically collects spectra at proscribed intervals of time. This routine is termed a continuous collection and is widely used in extractive FT-IR applications. The MDGrams/32™ routine that performs this task is called kinetic scanning.

In a kinetic scanning, the process for setting up the instrumentation is the same as was used for collecting calibration data or individual sample spectra. Sections III.D.1.a through III.D.1.c are therefore similar to the respective sections presented earlier. The remainder of the sections here have been modified significantly and should be reviewed carefully.

a) Setting instrument parameters.

As mentioned in the previous sections, consideration of the process being monitored should drive all decisions concerning data collection parameters *and then the same parameters should be used for the collection of calibration and sample spectra*. Setting parameters for the sample spectra is done in the same fashion as was used to set the parameters for the calibration data collection. Figure III.B.1 shows the *Parameter Settings* menu (|Collect|Parameter Settings) within MDGrams/32™. As can be seen in Figure III.B.1, this menu includes not only instrument parameters, but also some file options as well.

From this menu the apodization function, FFT zero filling, number of coadded scans, spectral range, data type, resolution, and gain can be set. Once these parameters are set, the values will remain as defaults until they are changed. As will be seen later, all of these parameters, excluding apodization function and FFT zero-filling, can also be changed within menus presented at the initiation of data collection scanning.

The *Instrument Configuration* button on this menu leads to a menu that allows the changing of fundamental instrument settings such as the laser wavelength. It should not be necessary to change these settings on the ASI/Demil FT-IR, and, therefore, these options will not be discussed.

b) Alignment of the instrument and gas cell.

The alignment of the instrument and gas cell can be checked using the alignment menu that is shown in Figure III.B.2. This menu can be accessed using the ALN button on the MDGrams/32™ main view, or from the Collect menu. The menu allows you to set the spectral range to view, data type to view, the resolution to use while scanning in align mode, and the gain to use during alignment. It is generally best to view align mode at 4 cm-1 resolution or lower so that any changes that may be made to the alignment are reflected immediately by a change in energy on the detector. It is also useful to check the alignment while viewing a single beam spectrum, displayed from 0 cm^{-1} to 8000 cm^{-1}. This allows the detector response envelope to be checked for any deviations from the norm.

Figure II.B.3 shows the MDGrams/32™ alignment screen. From this screen, the detector envelope and the relative amount of energy on the detector can be monitored. The amount of energy incident upon the detector is shown as a percentage of the capacity of the analog-to-digital converter (ADC). This number should be maximized whenever collecting data. It is preferable to have at least 50% for the collection of spectra; ADC filling percentages in the 80%-90% region are optimal.

All of the instrument and gas cell components are hard mounted into place within the enclosure of the ASI/Demil FT-IR system and the optical alignment of the system should not change in routine use. Mis-alignment is evidenced by low energy on the detector and, possibly, noticeable differences in the appearance of the single-beam spectra collected. Section II of this manual details steps for aligning the gas cell and FT-IR system.

c) Setting the flow parameters and purging the gas cell.

The ASI/Demil FT-IR system is equipped with an Alicat PVU-10SLPM-S flow/pressure/temperature sensor at the input of the gas cell. This sensor will be the basis for setting the flow parameters.

The following procedure should be accomplished using nitrogen gas only until the flow system is set at a known and controllable pressure and flow rate.

Initially, the valve on the exit of the gas cell and the valve on the gas delivery regulator should be closed. The regulator on the nitrogen cylinder should be set to deliver a pressure of approximately 15 psig.

First, set the display on the Alicat sensor to show the flow rate in liters/minute. Next, completely open the valve on the exit of the gas cell. Then, slowly, open the exit valve on the gas regulator until the Alicat sensor shows a flow rate of 3 liters/minute. When the flow rate has been achieved, switch the Alicat sensor to display the pressure in torr. Slowly begin to close the valve on the exit of the gas cell while monitoring the pressure on the Alicat sensor. Quit turning the exit valve when the pressure in the system has reached 800 torr. Now switch the Alicat sensor to display flow rate again. If the flow rate has changed drastically, it may be necessary to iterate the valve adjustment process until the desired flow rate and pressure can be achieved.

Once the desired flow rate and pressure have been established, note the delivery pressure on the nitrogen regulator. If the valves are not adjusted, this delivery pressure should get the system close to 3 liters/minute and 800 torr with most gases that will be flowed through the system. Once a new gas is flowing in the system, the valves can be adjusted to fine tune the systems flow rate and pressure. This procedure can be followed to achieve any desired set of flow parameters. The values of 3 liters/minute flow rate and 800 torr system pressure are common parameter settings used in extractive FT-IR. Different experiments may require different parameters.

An experiment was performed to determine the amount of time that the gases should be flowed through the cell in order to achieve a satisfactorily complete turn-over of the cell contents. The details of this experiment are presented in Appendix D of this manual.

d) Collecting a background Single Beam Spectrum.

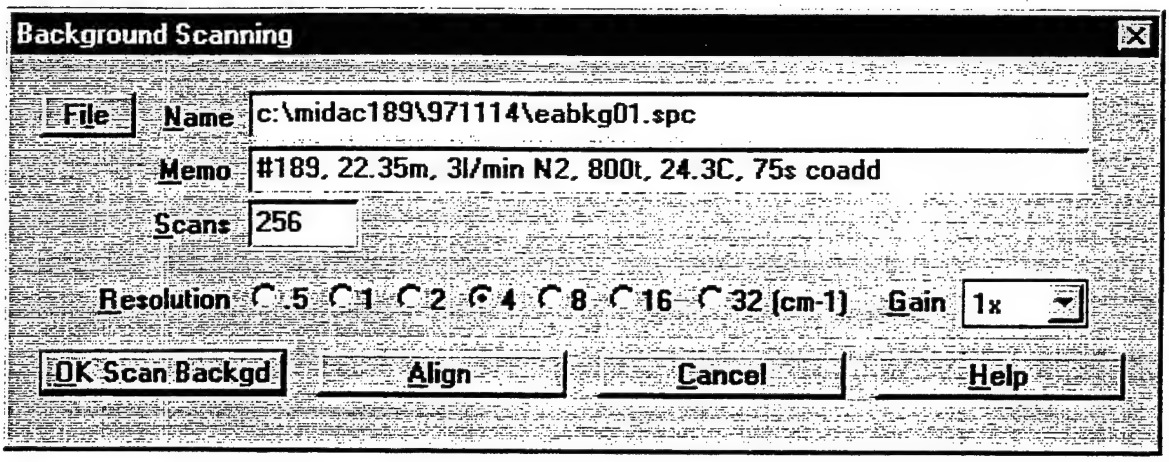
When performing a continuous collection, it is generally not practical to store both sample single beam spectra and sample absorbance spectra. Therefore, the samples are usually collected simply as absorbance spectra. In order to accomplish this, the background single beam spectrum must be collected using the *Background Scanning Menu* in MDGrams/32™. This menu can be accessed using the BKG button at the top of the MDGrams/32™ main view or from the Collect menu. The *Background Scanning Menu* is shown in Figure III.D.1.

This menu allows the user to enter a name for the background single beam and a unique memo that is stored in the file header. The user can also select the instrument resolution, number of coadded scans and the instrument gain to be used in collection of the background single beam spectrum.

Once the correct information has been entered, click on OK and the instrument will begin to collect the spectrum. The background scanning view will be displayed. This view will look exactly like the normal scanning view that is illustrated in Figure III.B.5.

Once the background spectrum is collected it will be stored to the hard disk, kept open in memory, and

Figure III.D.1 The Background Scanning Menu in MDGrams/32™.



automatically assigned as the background for subsequent use in creating absorbance spectra until a new background is collected or selected by the user.

In a continuous collection, a new background single beam should be collected at every opportunity. This will minimize the effects of instrument drift and result in higher quality data being collected. Ideally a background single beam would be collected every hour.

e) Collecting QA/QC data.

The collection of QA/QC data is critical in the process of continuous collections. QA/QC data not only indicates the quality of the sample spectra being collected, but also the quality of the background single beam spectrum used to create the sample absorbance spectra. The QA/QC data can be an indicator of instrument drift and tell the user when a new background single beam is required.

The collection of QA/QC data during a continuous collection can be performed in two ways. First, the continuous collection can be stopped, the gas cell purged with nitrogen, a new background collected, and a QA/QC sample collected and analyzed or, preferably, the QA/QC sample can be introduced into the sampling system while the sample analyte is flowing.

The advantage of the first method is that the QA/QC sample is treated exactly as it was in the laboratory when the QA/QC reference spectrum was created. This method should be employed at the beginning of a new continuous collection and then used as a trouble shooting tool. That is to say that if problems occur during the collection, a QA/QC sample should be measured in order to help determine if the problem is with the instrument or the gas sampling system.

The second method of collecting QA/QC data is useful because multiple QA/QC sample spectra can be collected in a short amount of time. This facilitates the calculation of instrument variance. Once the instrument variance is determined, any variance in the sample concentrations that is over and above the instrument variance can be attributed to the process being monitored. This is a valuable tool for characterizing a given process.

By definition, the QA/QC compound has absorbance features in the same region as the analyte molecules so the QA/QC sample could be a potential interferant for analyte molecules. Generally this is not a problem when using an automated spectral interpretation routine to analyze spectra and can validate performance of the spectral analysis algorithm for compounds with overlapping bands.

The actual collection of the QA/QC sample spectra will depend on the method used for the QA/QC procedure. If the QA/QC sample is run individually, the procedure to collect the spectrum is the same as outlined in Section III.C.1.e.

If the second method of collecting QA/QC data is employed, the QA/QC sample will become part of the actual sample, and the QA/QC data will automatically be collected with the sample spectra.

f) Collecting a sample spectrum.

As indicated earlier, the collection of sample absorbance spectra for a continuous collection is carried

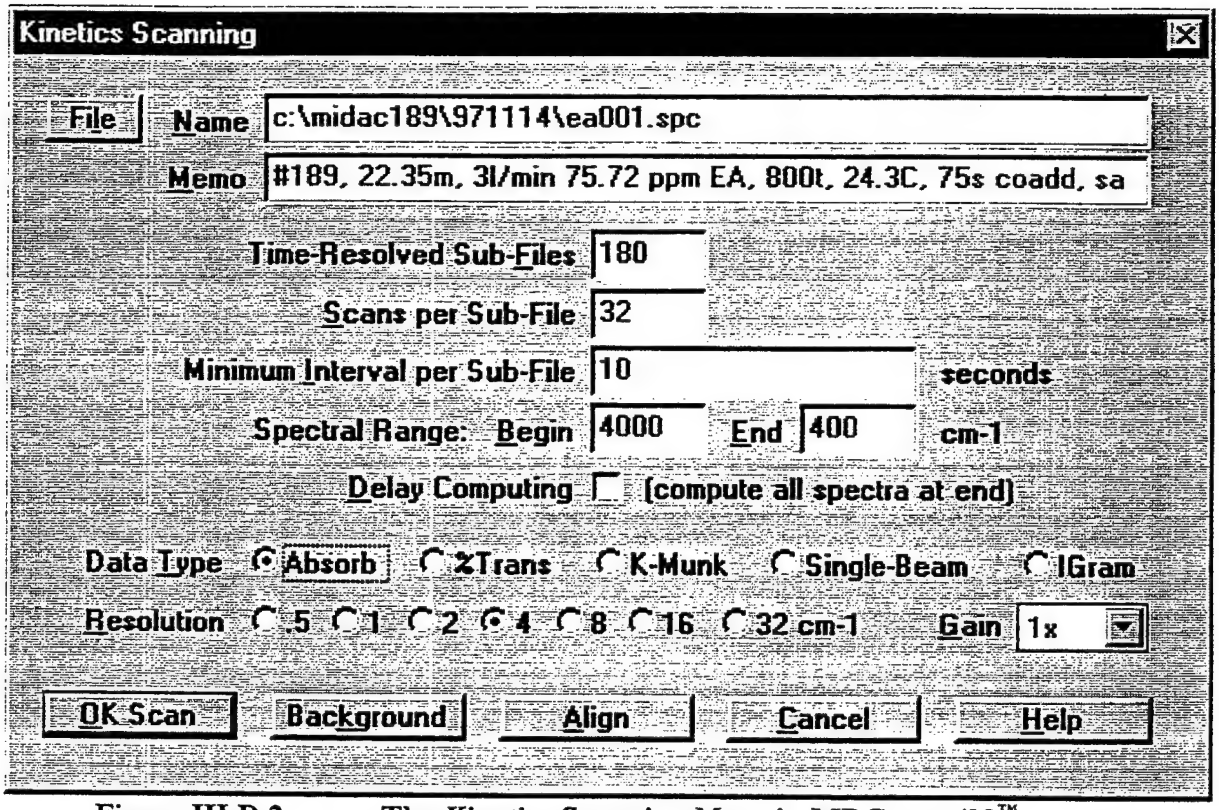


Figure III.D.2 The *Kinetics Scanning Menu* in MDGrams/32™

out in MDGrams/32™ by a routine called *Kinetic Scanning*. This routine is accessed either from the Collect Menu or from the KSC button on the button bar. The *Kinetics scanning* menu is shown in Figure III.D.2.

The *Kinetic Scanning Menu* allow the user to set the normal file options such as name and memo, but also allow the user to set the number of individual spectra that the file will hold. MDGrams/32™ calls this type of file a multifile. A multifile holds some number of individual spectra that are separated by some variable (i.e. time). In the example shown in Figure III.D.2, the file ea001.spc will contain 180 spectra that were collected at 10 second intervals. Each file will be an absorbance spectrum created from 32 co-added scans collected at 4 cm^{-1} resolution over the 400-4000 cm^{-1} spectral region, and at a gain of 1.

The other option on this menu is Delay Computing. This option allows the user to choose between collecting all of the spectra and then having MDGrams/32™ process (i.e. calculate absorbance) them all at the end of the data collection, or having MDGrams/32™ process each spectrum as it is collected. This last option is useful because it allows the user to see the spectra as they are collected.

Once the file and collection parameters have been specified, clicking on the OK button will start the kinetic scan. The kinetic scan view is shown in Figure III.D.3. This view will periodically update the displayed spectrum so that the spectrum that the user sees is only a few seconds old. By clicking on the MENU button at the bottom left of the view, the user can:

- stop scanning, which saves the file at the point of stopping, - abort the scanning, which stops scanning and does not save the spectra collected to that point,
- continue scanning, or
- hide the scanning in the background while performing other tasks on the computer.

g) Analyzing sample spectra.

Perform a manual spectral subtraction on all of the spectra collected in any given continuous collection project would be a daunting task. Therefore, the data from continuous collections are generally analyzed using automated routines. In this case, Midac AutoQuant™ will be employed to perform a batch analysis of the spectra collected using MDGrams/32™ kinetic scanning. This section will cover the preparation of those spectra within MDGrams/32™ for the batch analysis routine in Midac AutoQuant™ and the following section will discuss the actual analysis of the spectra.

In order to analyze spectra that are collected using MDGrams/32™ kinetic scanning with Midac AutoQuant™

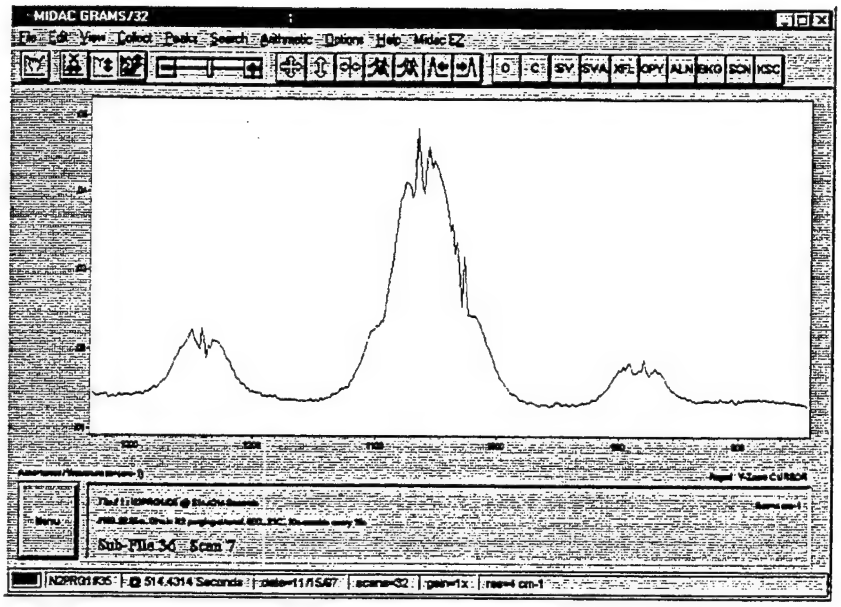


Figure III.D.3 The kinetic scanning view in MDGrams/32™

the spectra that are contained in the multifile must first be broken into the individual spectra that were collected. An array basic routine called MFU.ab will be used to perform this function. *MFU.ab* is accessed using the MFU user defined button at the bottom right-hand side of the MDGrams/32™ main view. Figure III.D.4 shows the MFU menu.

The option that will be used to split the multifile into single spectra for Midac AutoQuant™ is "Split into Singles". Once this option is selected, the user will be prompted to choose between overwriting the existing filename or choosing a new base filename for the individual spectra. It is recommended that a new base name be selected. MDGrams/32™ will increment the name automatically as it splits files out of the multifile. After the new base name is entered, MDGrams/32™ will prompt the user to verify that the file is to be split into the number of files that the program detects within the multifile. Click OK at this prompt, and MDGrams/32™ will begin to split the multifile into individual spectra that can be analyzed by Midac AutoQuant™.

III.E Performing Batch Data Analysis

III.E.1 Midac AutoQuant™

One of the attractive features of Midac AutoQuant™ is *Batch Analysis.* This feature allows the user to post-process data that were collected but not analyzed immediately. This feature also allows different analytical methods to be developed and tested on the same set of sample spectra.

Batch analysis is an effective and efficient means to analyze large amounts of data. Once the analytical method has been created, the program can be allowed to run through an entire directory full of spectra.

a) Creating an analytical method

The heart of the data analysis in Midac AutoQuant™ is the analytical method. The analytical method sets the calibration spectra and their associated parameters that are used to perform an analysis and the analytical regions that are used in the analysis.

In order to create an analytical method in Midac AutoQuant™, click on the New Method tab at the bottom of

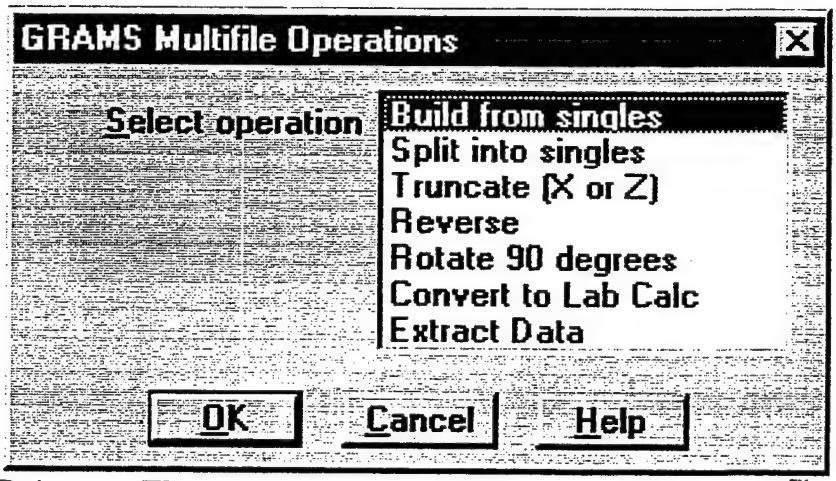


Figure III.D.4 The main menu of the MFU.ab in MDGrams/32™

the main view of Midac AutoQuant™ (Figure III.A.2) . This will open a menu that will allow the new method to benamed, a method description to be entered, and the computer path to be set. Once these file parameters are set, click on OK and the *Method Editor* will be displayed. The Midac AutoQuant™ *Method Editor* is shown in Figure III.D.1.

It is critical that the analytical method contains calibration sample spectra for not just the analytes of interest but also any compounds with absorption bands that may overlap with the analyte bands. If the method does not contain all of the components required to model the analyte sample spectrum, the coefficients of the calibration sample spectra that are in the method will be adjusted in an attempt to compensate for this deficiency, and, therefore, all of the analytical results obtained in that analysis will be in error.

Once the calibration sample spectra to be included in the analytical method have been determined, click on the Add file button. This will open a file list that allows the user to choose from the files stored on disk. Double click on the spectrum that is being added to the method. This places the description from the memo associated with that file in the active window of the Method Editor. It is wise to change this description to a one word descriptor because this is the description that will be used in the concentration vs time data that will be generated later.

Once the calibration spectrum is added to the analytical method, the file parameters must be set. First, enter the concentration of the calibration sample spectrum in the units of ppm*m. After the concentration is added, add the alarm concentration for that particular compound in the process that is being monitored. Next, click on the Add button at the bottom right of the Method Editor. This button will cause a small window to pop up, within which the analytical region can be assigned for the active calibration sample spectrum. Enter the analytical region that has been determined for the active compound. If there is more than one analytical region to be used, keep hitting add until all regions are entered into the method.

After the file specifications are set, the method parameters must be set. click on the Parameters button at the top right of the Method Editor. This will display the Parameters window. There are really just two parameters that need to be changed when performing a batch analysis. The first is the pathlength. The pathlength can be set to a value of 1 and the answer that is displayed in the concentration versus time plot will be in ppm*m. Or, the actual pathlength used can be entered and the concentration units on the concentration versus time plot will be ppm.

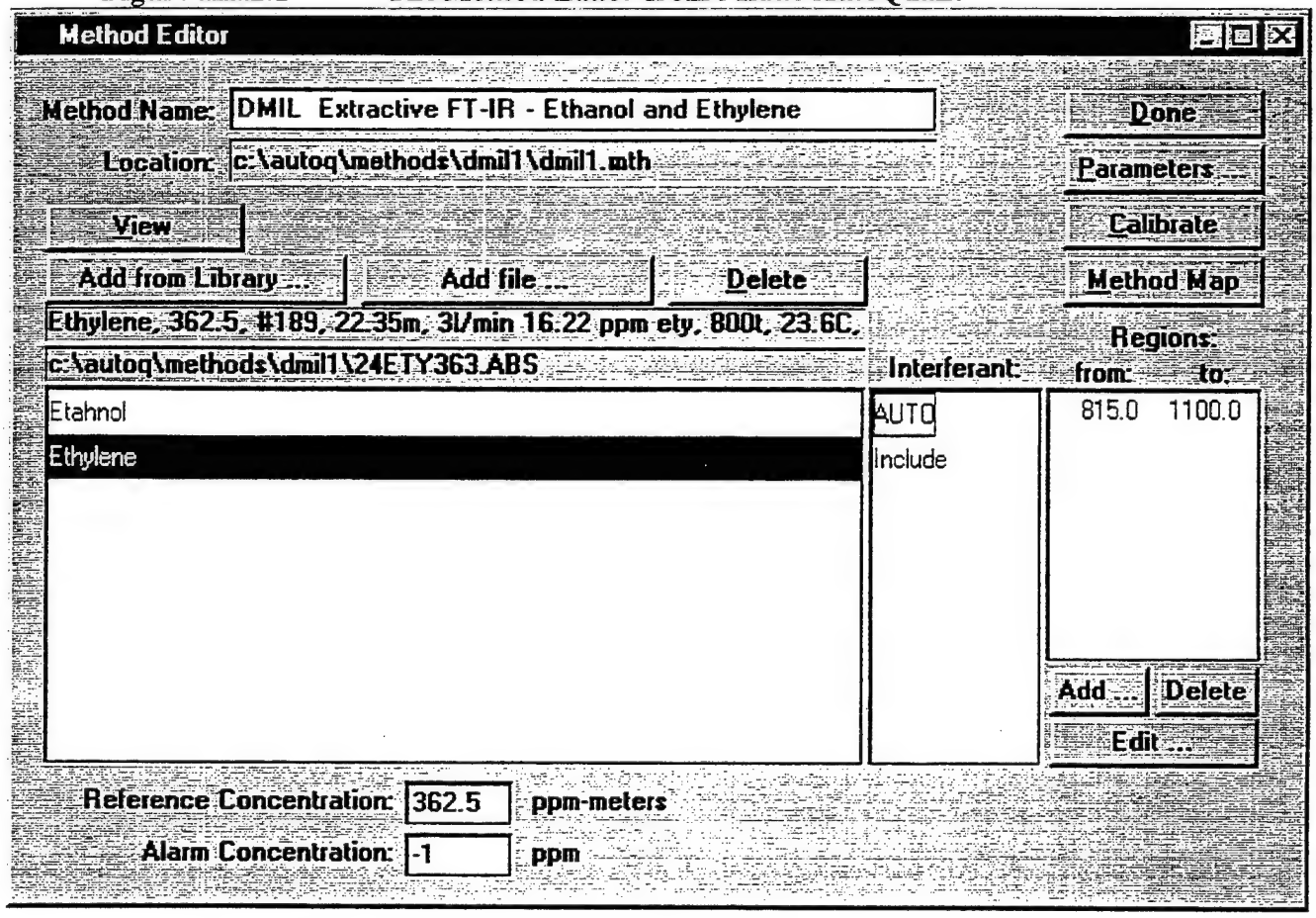
After the pathlength is entered, the baseline correction function should be determined. Ideally, this function will not be required, but most often a baseline correction is required. It must be noted that when analyzing spectra collected in MDGrams/32™, the sample spectrum must be Mean Centered. This is because of differences in how MDGrams/32™ and Midac AutoQuant™ perform the FFT on their individual data formats.

After the method parameters have been set, the method must be calibrated. The calibration of the method simply creates the matrices that the method uses to analyze sample spectra. Click on Calibrate, and a screen pops up that shows the method being calibrated. When finished, Midac AutoQuant™ will ask to either close the window or print the results. The analytical method is now complete. Close the calibration results window and press done on the Method Editor. This returns the display to the main view of Midac AutoQuant™.

b) Performing the batch analysis

The *Batch Analysis Menu* is shown in Figure III.E.2. This menu allows the user to select any or all

Figure III.E.1 The *Method Editor* from Midac AutoQuant™



spectra within a given directory for analysis by the analytical method that is shown at the bottom of the menu. Once the files to be analyzed are selected, click Analyze. At this point, the Batch Analysis menu shown in Figure III.E.3 appears. This menu determines if the residual spectrum is saved for viewing by the user. The residual spectrum is the spectrum that remains after the subtraction of the algorithm's suggested spectrum from the real spectrum. If the analysis is correct, this spectrum will be made up exclusively of noise in the analytical regions that were specified by the analytical method. This spectrum should be saved for viewing because it is the best tool available for the evaluation of the analysis results.

Once the path for the residual spectrum is set, the batch analysis is started by clicking the Start button.

c) Evaluating the results of the batch analysis

Figure III.E.4 is the *Batch Analysis Results* view. This view shows a plot of concentration versus time at the top, a table of results at the bottom left, and the spectrum display at the bottom right. There are two things to note here. First, the analysis is not performed in sequential order on the selected data. As the table of results shows, Midac AutoQuant™ starts with a random spectra out of the selected spectra. This is not a big problem, but is a source of irritation when plotting the analysis results in Microsoft® Excel'97. The second thing to note is that the concentration versus time plot does not always appear when performing a batch analysis. This is a bug in the programming.

The spectrum display is where the residual spectrum should be viewed to determine how well the analysis worked. Ideally, the error that is listed in the table of results would be the main indication of the quality of the results. However, because of the way that Midac AutoQuant™ performs the baseline correction and the subsequent subtraction of the analytical regions, this error is not always correct. Therefore, viewing the residual spectrum for indications of any analyte or interferant that is still present in the residual spectrum is the best evaluation of the batch analysis results.

d) Plotting the results of the batch analysis

Microsoft® Excel '97 is used to plot the results of

the batch analysis. In order to get the results into Microsoft® Excel '97 (the result table shown in the Figure III.E.4), click on the Save button. This will prompt the user to specify an file path and filename for a text file that contains the results table. Once this text file is written, the data can be imported into Microsoft® Excel '97.

Microsoft® Excel '97 will automatically import the text file when it is opened from the File menu. Once the text file is imported, it should be save as a Microsoft® Excel '97 file for the purposes of archiving.

In Microsoft® Excel '97 the first operation that should be performed is to sort the data. To do this, highlight the entire block of cells that contains the batch analysis results and click |Data|Sort Descending. This will order the results in the proper sequence.

After the results are in the proper sequence, the next step is to write the associated file time in the second column. This is required because all of the files are broken from the same MDGrams/32™ multifile and all of the individual spectra are assigned the same time. In order to plot the data on the proper time scale, the correct times must be entered into the spreadsheet.

The easiest way to perform this task is to highlight the cells that contain the incorrect time marks and delete these values. Next, insert the correct time for the first and second samples. It may be required to change the cell format to accept the hh:mm:ss time format. This is done in the under the |Format|Cells|Numbers menu. Remember that the kinetic scan was collected at constant time interval. So, after the first to times are entered, highlight these two times and the remaining cells that need to be filled with times. Next, click on the |Edit|Fill menu and choose Series. This function automatically detects the time interval and fills the highlighted cells with the proper times. Once the proper times are entered into the spreadsheet, a chart showing concentration versus time data for each analyte can be created using standard Microsoft® Excel '97 functions.

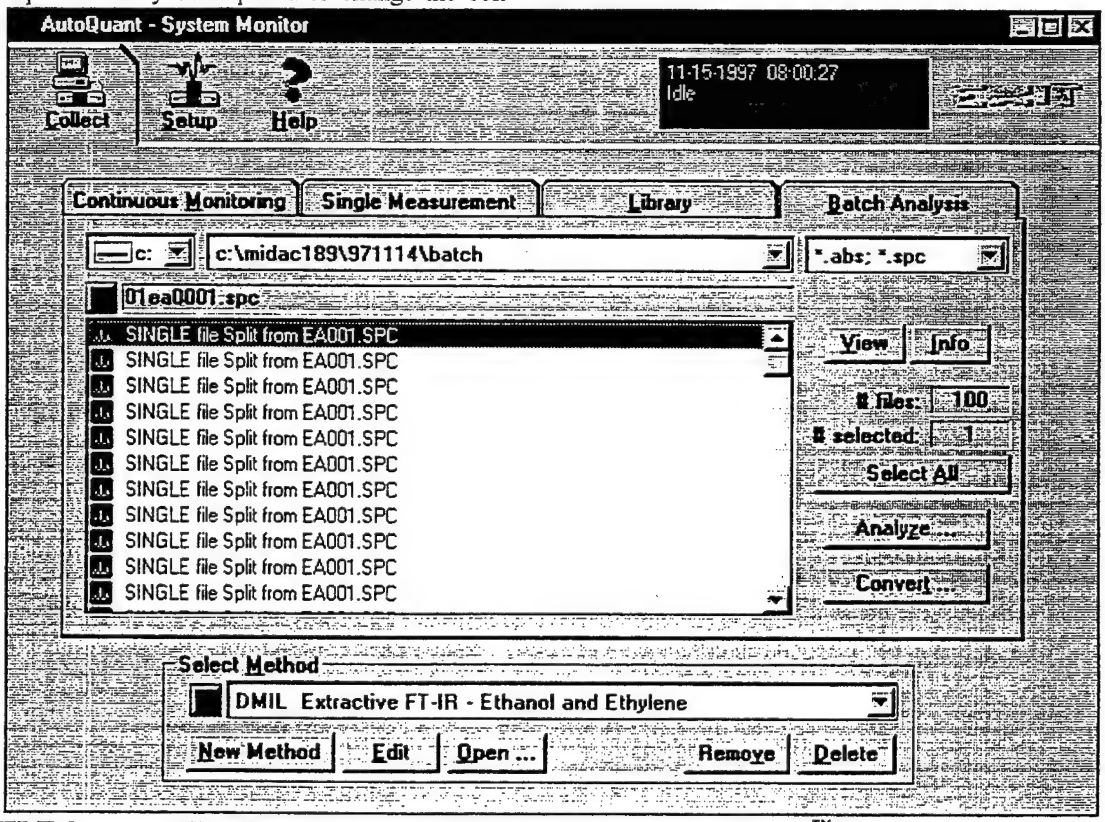


Figure III.E.2 The *Batch Analysis Menu* in Midac AutoQuant™.

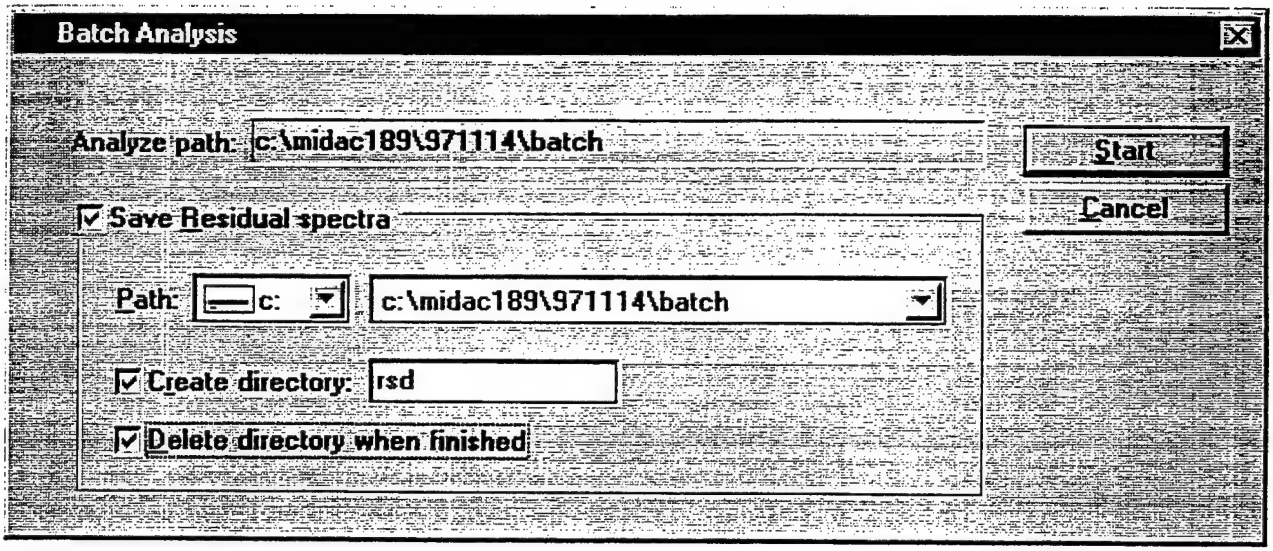
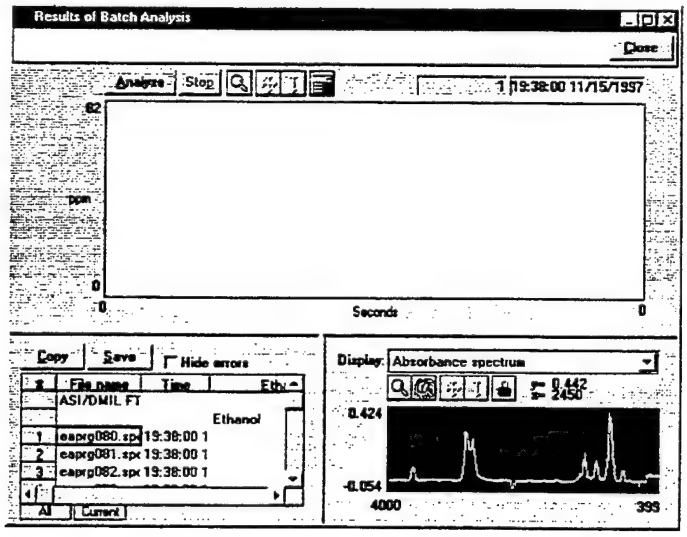


Figure III.E.3 The residual spectrum menu in Midac AutoQuant™

Figure III.E.4 The *Batch Analysis Results* view in Midac AutoQuant™



Appendix A: Hardware and Software Delivered by AeroSurvey, Inc.

The following tables list the hardware and software that was delivered by AeroSurvey, Inc. to Edgewood Research Development and Engineering Center in Aberdeen Proving Ground, MD on November 18, 1997. These tables are broken into components that have been integrated into the modified extractive FT-IR system and components that are not integrated into the modified extractive FT-IR system.

The original equipment that was supplied by ERDEC was assembled by Apogee Scientific, Inc. of Denver, CO. Much of this equipment was assembled in house and was not assigned a serial number.

The equipment that was supplied by Midwest Research Institute was done in order to help ensure delivery of a more workable system because this system is planned for use under a separate contract by MRI. MRI supplied this equipment in kind and ownership of this equipment is governed by MRI contracts and policies.

Table 1. Components delivered by AeroSurvey that have been integrated into the modified extractive FT-IR spectrometer and software package.

Description	Serial/License #	Original Supplier
Midac interferometer block and associated electronics	#189	ERDEC
EG&G Judson MCT detector	J15D16-M964-801M-55-Midac	ERDEC
Laser alignment assembly fabricated by AeroSurvey	NA	ERDEC
Spectrometer housing fabricated by AeroSurvey	NA	ERDEC
Infrared Analysis, Inc. Model 35-V variable path White cell	MR930722	MRI
Dell XPS266 desktop computer	BRX34	MRI
Dell D1025HTX 17" monitor	8048271	MRI
Midac - AutoQuant version 2.07	1097120201	ERDEC
Midac - AutoQuant version 2.08	NA	ERDEC
MicroSoft - Excel '97	001004M0509A401565	MRI/ERDEC
Galactic Industries - MDGrams/32 Version 4.1	G241110149701-109701	ERDEC
Alicat pressure/temperature/flow sensor - PVU-10SLPM-S	3224	ERDEC

Table 2. Components delivered by AeroSurvey that are not integrated into the modified extractive FT-IR spectrometer and software package.

Description	Serial/License #	Original Supplier
Midac interferometer case	189	ERDEC
Inteferometer housing fabricated by Apogee Scientific	NA	ERDEC
Laser alignment assembly fabricated by Apogee Scientific	NA	ERDEC
Flow-through sample cell fabricated by Apogee Scientific	NA	ERDEC
Liquid nitrogen fill system fabricated by Apogee Scientific	NA	ERDEC
External field mirror assembly fabricated by Apogee Scientific	NA	ERDEC
DTK PEER 1660 desktop computer	NA	ERDEC
CTX CVP-5468NI 14" monitor	A50-30401424	ERDEC

Appendix B:

PROTOCOL FOR THE USE OF EXTRACTIVE FOURIER TRANSFORM INFRARED (FT-IR) SPECTROMETRY FOR THE ANALYSES OF GASEOUS EMISSIONS FROM STATIONARY SOURCES

PROTOCOL FOR THE USE OF EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY FOR THE ANALYSES OF GASEOUS EMISSIONS FROM STATIONARY SOURCES

INTRODUCTION

The purpose of this document is to set general guidelines for the use of modern FTIR spectroscopic methods for the analysis of gas samples extracted from the effluent of stationary emission sources. This document outlines techniques for developing and evaluating such methods and sets basic requirements for reporting and quality assurance procedures.

1.0 NOMENCLATURE

1.1 Appendix A lists definitions of the symbols and terms used in this Protocol, many of which have been taken directly from American Society for Testing and Materials (ASTM) publication E 131-90a, entitled "Terminology Relating to Molecular Spectroscopy."

1.2 Except in the case of background spectra or where otherwise noted, the term "spectrum" refers to a double-beam spectrum in units of absorbance vs. wavenumber (cm^{-1}).

1.3 The term "Study" in this document refers to a publication that has been subjected to EPA- or peer-review.

2.0 APPLICABILITY AND ANALYTICAL PRINCIPLE

2.1 Applicability. This Protocol applies to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam absorption spectroscopy in the mid-infrared band. It does not specifically address other FTIR applications, such as single-beam spectroscopy, analysis of open-path (non-enclosed) samples, and continuous measurement techniques. If multiple spectrometers, absorption cells, or instrumental linewidths are used in such analyses, each distinct operational configuration of the system must be evaluated separately according to this Protocol.

2.2 Analytical Principle.

2.2.1 In the mid-infrared band, most molecules exhibit characteristic gas phase absorption spectra that may be recorded by FTIR systems. Such systems consist of a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements for the transfer of infrared radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling the instrument, processing the signal, and for performing both Fourier transforms and quantitative analyses of spectral data.

2.2.2 The absorption spectra of pure gases and of mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern FTIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. Reference A describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

3.0 GENERAL PRINCIPLES OF PROTOCOL REQUIREMENTS

The characteristics that distinguish FTIR systems from gas analyzers used in instrumental gas analysis methods (e.g., EPA Methods 6C and 7E) are: (1) Computers are necessary to obtain and analyze data; (2) chemical concentrations can be quantified using previously recorded infrared reference spectra; and (3) analytical assumptions and results, including possible effects of interfering compounds, can be evaluated after the quantitative analysis. The following general principles and requirements of this Protocol are based on these characteristics.

3.1 Verifiability and Reproducibility of Results. Store all data and document data analysis techniques sufficient to allow an independent agent to reproduce the analytical results from the raw interferometric data.

3.2 Transfer of Reference Spectra. To determine whether reference spectra recorded under one set of conditions (e.g., optical bench, instrumental linewidth, absorption pathlength, detector performance, pressure, and temperature) can be used to analyze sample spectra taken under a different set of conditions, quantitatively compare "calibration transfer standards" (CTS) and reference spectra as described in this Protocol. (Note: The CTS may, but need not, include analytes of interest). To effect this, record the absorption spectra of the CTS (a) immediately before and immediately after recording reference spectra and (b) immediately after recording sample spectra.

3.3 Evaluation of FTIR Analyses. The applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes:

3.3.1 Sample-Independent Factors. Examples are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference absorption spectra, and type of mathematical analyses of the spectra. These factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available. For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Similarly, the accuracy of measurements may be estimated from the analysis of the reference spectra.

3.3.2 Sample-Dependent Factors. Examples are spectral interferants (e.g., water vapor and CO_2) or the overlap of spectral features of different compounds and contamination deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferants (a standard inital step) and analysis of samples (includes effect of other analytical errors) are necessary. Thus, the Protocol requires post-analysis calculation of measurement concentration uncertainties for the detection of these potential sources of measurement error.

4.0 PRE-TEST PREPARATIONS AND EVALUATIONS

Before testing, demonstrate the suitability of FTIR spectrometry for the desired application according to the procedures of this section.

4.1 Identify Test Requirements. Identify and record the test requirements described below in 4.1.1 through 4.1.5. These values set

the desired or required goals of the proposed analysis; the description of methods for determining whether these goals are actually met during the analysis comprises the majority of this Protocol.

4.1.1 Analytes (specific chemical species) of interest. Label the analytes from i = 1 to I.

4.1.2 Analytical uncertainty limit (AU_i). The AU_i is the maximum permissible fractional uncertainty of analysis for the i^{th} analyte concentration, expressed as a fraction of the analyte concentration in the sample.

4.1.3 Required detection limit for each analyte (DL_i, ppm). The detection limit is the lowest concentration of an analyte for which its overall fractional uncertainty (OFU_i) is required to be less than its analytical uncertainty limit (AU_i).

4.1.4 Maximum expected concentration of each analyte ($CMAX_i$, ppm).

4.2 Identify Potential Interferants. Considering the chemistry of the process or results of previous Studies, identify potential interferants, i.e., the major effluent constituents and any relatively minor effluent constituents that possess either strong absorption characteristics or strong structural similarities to any analyte of interest. Label them 1 through N_j, where the subscript "j" pertains to potential interferants. Estimate the concentrations of these compounds in the effluent ($CPOT_j$, ppm).

4.3 Select and Evaluate the Sampling System. Considering the source, e.g., temperature and pressure profiles, moisture content, analyte characteristics, and particulate concentration), select the equipment for extracting gas samples. Recommended are a particulate filter, heating system to maintain sample temperature above the dew point for all sample constituents at all points within the sampling system (including the filter), and sample conditioning system (e.g., coolers, water-permeable membranes that remove water or other compounds from the sample, and dilution devices) to remove spectral interferants or to protect the sampling and analytical components. Determine the minimum absolute sample system pressure (P_{min}, mmHg) and the infrared absorption cell volume (V_{SS}, liter). Select the techniques and/or equipment for the measurement of sample pressures and temperatures.

4.4 Select Spectroscopic System. Select a spectroscopic configuration for the application. Approximate the absorption pathlength (L_S', meter), sample pressure (P_S', kPa), absolute sample temperature T_S', and signal integration period (t_{SS}, seconds) for the analysis. Specify the nominal minimum instrumental linewidth (MIL) of the system. Verify that the fractional error at the approximate values P_S' and T_S' is less than one half the smallest value AU_i (see Section 4.1.2).

4.5 Select Calibration Transfer Standards (CTS's). Select CTS's that meet the criteria listed in Sections 4.5.1, 4.5.2, and 4.5.3.

> Note: It may be necessary to choose preliminary analytical regions (see Section 4.7), identify the minimum analyte linewidths, or estimate the system noise level (see Section 4.12) before selecting the CTS. More than one compound may be needed to meet the criteria; if so, obtain separate cylinders for each compound.

4.5.1 The central wavenumber position of each analytical region lies within 25 percent of the wavenumber position of at least one CTS absorption band.

4.5.2 The absorption bands in 4.5.1 exhibit peak absorbances greater than ten times the value RMS_{EST} (see Section 4.12) but less than 1.5 absorbance units.

4.5.3 At least one absorption CTS band within the operating range of the FTIR instrument has an instrument-independent linewidth no greater than the narrowest analyte absorption band; perform and document measurements or cite Studies to determine analyte and CTS compound linewidths.

4.5.4 For each analytical region, specify the upper and lower wavenumber positions (FFU_m and FFL_m, respectively) that bracket the CTS absorption band or bands for the associated analytical region. Specify the wavenumber range, FNU to FNL, containing the absorption band that meets the criterion of Section 4.5.3.

4.5.5 Associate, whenever possible, a single set of CTS gas cylinders with a set of reference spectra. Replacement CTS gas cylinders shall contain the same compounds at concentrations within 5 percent of that of the original CTS cylinders; the entire absorption spectra (not individual spectral segments) of the replacement gas shall be scaled by a factor between 0.95 and 1.05 to match the original CTS spectra.

4.6 Prepare Reference Spectra.

Note: Reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board; they may be used if applicable.

4.6.1 Select the reference absorption pathlength (L_R) of the cell.

4.6.2 Obtain or prepare a set of chemical standards for each analyte, potential and known spectral interferants, and CTS. Select the concentrations of the chemical standards to correspond to the top of the desired range.

4.6.2.1 Commercially-Prepared Chemical Standards. Chemical standards for many compounds may be obtained from independent sources, such as a specialty gas manufacturer, chemical company, or commercial laboratory. These standards (accurate to within ±2 percent) shall be prepared according to EPA Protocol 1 (see Reference D) or shall be traceable to NIST standards. Obtain from the supplier an estimate of the stability of the analyte concentration; obtain and follow all the supplier's recommendations for recertifying the analyte concentration.

4.6.2.2 Self-Prepared Chemical Standards. Chemical standards may be prepared as follows: Dilute certified commercially prepared chemical gases or pure analytes with ultra-pure carrier (UPC) grade nitrogen according to the barometric and volumetric techniques generally described in Reference A, Section A4.6.

4.6.3 Record a set of the absorption spectra of the CTS {R1}, then a set of the reference spectra at two or more concentrations in duplicate over the desired range (the top of the range must be less than 10 times that of the bottom), followed by a second set of CTS spectra {R2}. (If self-prepared standards are used, see Section 4.6.5 before disposing of any of the standards.) The maximum accepted standard concentration-pathlength product (ASCPP) for each compound shall be higher than the maximum estimated concentration-pathlength products for both analytes and known interferants in the effluent gas. For each analyte, the minimum ASCPP shall be no greater than ten times the concentration-

pathlength product of that analyte at its required detection limit.

4.6.4 Permanently store the background and interferograms in digitized form. Document details of the mathematical process for generating the spectra from these interferograms. Record the sample pressure (P_R), sample temperature (T_R), reference absorption pathlength (L_R), and interferogram signal integration period (t_{SR}). Signal integration periods for the background interferograms shall be $\geq t_{SR}$. Values of P_R, L_R, and t_{SR} shall not deviate by more than ±1 percent from the time of recording {R1} to that of recording {R2}.

4.6.5 If self-prepared chemical standards are employed and spectra of only two concentrations are recorded for one or more compounds, verify the accuracy of the dilution technique by analyzing the prepared standards for those compounds with a secondary (non-FTIR) technique as follows:

4.6.5.1 Record the response of the secondary technique to each of the four standards prepared.

4.6.5.2 Perform a linear regression of the response values (dependant variable) versus the accepted standard concentration (ASC) values (independent variable), with the regression constrained to pass through the zero-response, zero ASC point.

4.6.5.3 Calculate the average fractional difference between the actual response values and the regression-predicted values (those calculated from the regression line using the four ASC values as the independent variable).

4.6.5.4 If the average fractional difference value calculated in Section 4.6.5.3 is larger for any compound than the corresponding AU_i, the dilution technique is not sufficiently accurate and the reference spectra prepared are not valid for the analysis.

4.7 Select Analytical Regions. Using the general considerations in Section 7 of Reference A and the spectral characteristics of the analytes and interferants, select the analytical regions for the application. Label them m = 1 to M. Specify the lower, center and upper wavenumber positions of each analytical region (FL_m, FC_m, and FU_m, respectively). Specify the analytes and interferants which exhibit absorption in each region.

4.8 Determine Fractional Reproducibility Uncertainties. Using Appendix E, calculate the fractional reproducibility uncertainty for each analyte (FRU_i) from a comparison of {R1} and {R2}. If $FRU_i > AU_i$ for any analyte, the reference spectra generated in Section 4.6 are not valid for the application.

4.9 Identify Known Interferants. Using Appendix B, determine which potential interferant affects the analyte concentration determinations. If it does, relabel the potential interferant as "known" interferant, and designate these compounds from k = 1 to K. Appendix B also provides criteria for determining whether the selected analytical regions are suitable.

4.10 Prepare Computerized Analytical Programs.

4.10.1 Choose or devise mathematical techniques (e.g, classical least squares, inverse least squares, cross-correlation, and factor analysis) based on Equation 4 of Reference A that are appropriate for analyzing spectral data by comparison with reference spectra.

4.10.2 Following the general recommendations of Reference A, prepare a computer program or set of programs that analyzes all the analytes and known

interferants, based on the selected analytical regions (4.7) and the prepared reference spectra (4.6). Specify the baseline correction technique (e.g., determining the slope and intercept of a linear baseline contribution in each analytical region) for each analytical region, including all relevant wavenumber positions.

4.10.3 Use programs that provide as output [at the reference absorption pathlength (L_R), reference gas temperature (T_R), and reference gas pressure (P_R)] the analyte concentrations, the known interferant concentrations, and the baseline slope and intercept values. If the sample absorption pathlength (L_S), sample gas temperature (T_S) or sample gas pressure (P_S) during the actual sample analyses differ from L_R, T_R, and P_R, use a program or set of programs that applies multiplicative corrections to the derived concentrations to account for these variations, and that provides as output both the corrected and uncorrected values. Include in the report of the analysis (see Section 7.0) the details of any transformations applied to the original reference spectra (e.g., differentiation), in such a fashion that all analytical results may be verified by an independent agent from the reference spectra and data spectra alone.

4.11 Determine the Fractional Calibration Uncertainty. Calculate the fractional calibration uncertainty for each analyte (FCU_i) according to Appendix F, and compare these values to the fractional uncertainty limits (AU_i; see Section 4.1). If $FCU_i > AU_i$), either the reference spectra or analytical programs for that analyte are unsuitable.

4.12 Verify System Configuration Suitability. Using Appendix C, measure or obtain estimates of the noise level (RMS_{EST}, absorbance) of the FTIR system; alternatively, construct the complete spectrometer system and determine the values RMS_{Sm} using Appendix G. Estimate the minimum measurement uncertainty for each analyte (MAU_i, ppm) and known interferant (MIU_k, ppm) using Appendix D. Verify that (a) $MAU_i < (AU_i)(DL_i)$, $FRU_i < AU_i$, and $FCU_i < AU_i$ for each analyte and that (b) the CTS chosen meets the requirements listed in Section 4.5.

5.0 SAMPLING AND ANALYSIS PROCEDURE

5.1 Analysis System Assembly and Leak-Test. Assemble the analysis system. Allow sufficient time for all system components to reach the desired temperature. Then determine the leak-rate (L_R) and leak volume (V_L), where $V_L = L_R\, t_{SS}$. Leak volumes shall be ≤4 percent of V_{SS}.

5.2 Verify Instrumental Performance. Measure the noise level of the system in each analytical region using the procedure of Appendix G. If any noise level is higher than that estimated for the system in Section 4.12, repeat the calculations of Appendix D and verify that the requirements of Section 4.12 are met; if they are not, adjust or repair the instrument and repeat this section.

5.3 Determine the Sample Absorption Pathlength. Record a background spectrum. Then, fill the absorption cell with CTS at the pressure P_R and record a set of CTS spectra {R3}. Store the background and unscaled CTS single beam interferograms and spectra. Using Appendix H, calculate the sample absorption pathlength (L_S) for each analytical region. The values L_S shall not differ from the approximated sample pathlength L_S' (see Section 4.4) by more than 5 percent.

5.4 Record Sample Spectrum. Connect the sample line to the source. Either evacuate the absorption cell to an absolute pressure below 5 mmHg before extracting a sample

from the effluent stream into the absorption cell, or pump at least ten cell volumes of sample through the cell before obtaining a sample. Record the sample pressure P_S. Generate the absorbance spectrum of the sample. Store the background and sample single beam interferograms, and document the process by which the absorbance spectra are generated from these data. (If necessary, apply the spectral transformations developed in Section 5.6.2). The resulting sample spectrum is referred to below as S_S.

Note: Multiple sample spectra may be recorded according to the procedures of Section 5.4 before performing Sections 5.5 and 5.6.

5.5 Quantify Analyte Concentrations. Calculate the unscaled analyte concentrations RUA_i and unscaled interferant concentrations RUI_K using the programs developed in Section 4. To correct for pathlength and pressure variations between the reference and sample spectra, calculate the scaling factor $R_{LPS} = (L_R P_R T_S)/(L_S P_S T_R)$. Calculate the final analyte and interferant concentrations $RSA_i = R_{LPS} RUA_i$ and $RSI_k = R_{LPS} RUI_k$.

5.6 Determine Fractional Analysis Uncertainty. Fill the absorption cell with CTS at the pressure P_S. Record a set of CTS spectra {R4}. Store the background and CTS single beam interferograms. Using Appendix H, calculate the fractional analysis uncertainty (FAU) for each analytical region. If the FAU indicated for any analytical region is larger than the required accuracy requirements determined in Section 4.1, then comparisons to previously recorded reference spectra are invalid in that analytical region, and the analyst shall perform one or both of the following procedures:

5.6.1 Perform instrumental checks and adjust the instrument to restore its performance to acceptable levels. If adjustments are made, repeat Sections 5.3, 5.4 (except for the recording of a sample spectrum), and 5.5 to demonstrate that acceptable uncertainties are obtained in all analytical regions.

5.6.2 Apply appropriate mathematical transformations (e.g., frequency shifting, zero-filling, apodization, smoothing) to the spectra (or to the interferograms upon which the spectra are based) generated during the performance of the procedures of Section 5.3. Document these transformations and their reproducibility. (how ?) Do not apply multiplicative scaling of the spectra, or any set of transformations that is mathematically equivalent to multiplicative scaling. Different transformations may be applied to different analytical regions. Frequency shifts shall be smaller than one-half the minimum instrumental linewidth, and must be applied to all spectral data points in an analytical region. The mathematical transformations may be retained for the analysis if they are also applied to the appropriate analytical regions of all sample spectra recorded, and if all original sample spectra are digitally stored. Repeat Sections 5.3, 5.4 (except the recording of a sample spectrum), and 5.5 to demonstrate that these transformations lead to acceptable calculated concentration uncertainties in all analytical regions.

6.0 POST-ANALYSIS EVALUATIONS

Estimate the overall accuracy of the analyses performed in Section 5 as follows:

6.1 Qualitatively Confirm the Assumed Matrix. Examine each analytical region of the sample spectrum for spectral evidence of unexpected or unidentified interferants. If found, identify the interfering compounds (see Reference C for guidance) and add them to the list of known interferants. Repeat the procedures of Section 4 to include the interferants in the uncertainty calculations and

analysis procedures. Verify that the MAU and FCU values do not increase beyond acceptable levels for the application requirements. Re-calculate the analyte concentrations (Section 5.5) in the affected analytical regions.

6.2 Quantitatively Evaluate Fractional Model Uncertainty (FMU). Perform the procedures of either Section 6.2.1 or 6.2.2:

6.2.1 Using Appendix I, determine the fractional model error (FMU) for each analyte.

6.2.2 Provide statistically determined uncertainties FMU for each analyte which are equivalent to two standard deviations at the 95% confidence level. Such determinations, if employed, must be based on mathematical examinations of the pertinent sample spectra (not the reference spectra alone). Include in the report of the analysis (see Section 7.0) a complete description of the determination of the concentration uncertainties.

6.3 Estimate Overall Concentration Uncertainty (OCU). Using Appendix J, determine the overall concentration uncertainty (OCU) for each analyte. If the OCU is larger than the required accuracy for any analyte, repeat Sections 4 and 6.

7.0 REPORTING REQUIREMENTS

[Documentation pertaining to virtually all the procedures of Sections 4, 5, and 6 will be required. Software copies of reference spectra and sample spectra will be retained for some minimum time following the actual testing.]

8.0 REFERENCES

A) Standard Practices for General Techniques of Infrared Quantitative Analysis (American Society for Testing and Materials, Designation E 168-88).

B) The Coblentz Society Specifications for Evaluation of Research Quality Analytical Infrared Reference Spectra (Class II); Anal. Chemistry 47, 945A (1975); **Appl. Spectroscopy 444, pp. 211-215, 1990.**

C) Standard Practices for General Techniques for Qualitative Infrared Analysis, American Society for Testing and Materials, Designation E 1252-88.

D) "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Emissions Monitors (Protocol Number 1)," June 1978, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods, EPA-600/4-77-027b, August 1977.

APPENDIX A

DEFINITIONS OF TERMS AND SYMBOLS

A.1 Definitions of Terms

absorption band - a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

absorption pathlength - in a spectrophotometer, the distance, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

analytical region - a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analyte.

> Note: The quantitative result for a single analyte may be based on data from more than one analytical region.

apodization - modification of the ILS function by multiplying the interferogram by a weighing function whose magnitude varies with retardation.

background spectrum - the single beam spectrum obtained with all system components without sample present.

baseline - any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beers's law - the direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration.

calibration transfer standard (CTS) gas - a gas standard of a
compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectra; see Section 4.5.1.

compound - a substance possessing a distinct, unique molecular structure.

concentration (c) - the quantity of a compound contained in a
unit quantity of sample. The unit "ppm" (number, or mole, basis) is recommended.

concentration-pathlength product - the mathematical product of concentration of the species and absorption pathlength. For reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's law. The units "centimeters-ppm" or "meters-ppm" are recommended.

derivative absorption spectrum - a plot of rate of change of absorbance or of any function of absorbance with respect to wavelength or any function of wavelength.

double beam spectrum - a transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

> Note: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected

at different times along the same absorption path.

fast Fourier transform (FFT) - a method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

flyback - interferometer motion during which no data are recorded.

Fourier transform (FT) - the mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

Fourier transform infrared (FTIR) spectrometer - an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency.

> Note: When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPCL/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.

frequency, ν - the number of cycles per unit time.

infrared - the portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

interferogram, I(σ) - record of the modulated component of the interference signal measured as a function of retardation by the detector.

interferometer - device that divides a beam of radiant energy into two or more paths, generate an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

linewidth - the full width at half maximum of an absorption band in units of wavenumbers (cm^{-1}).

mid-infrared - the region of the electromagnetic spectrum from approximately 400 to 5000 cm^{-1}.

reference spectra - absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

retardation, σ - optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation."

scan - digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

scaling - application of a multiplicative factor to the absorbance values in a spectrum.

single beam spectrum - Fourier-transformed interferogram, representing the detector response vs. wavenumber.

> Note: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum"

above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.

standard reference material - a reference material, the composition or properties of which are certified by a recognized standardizing agency or group.

Note: The equivalent ISO term is "certified reference material."

transmittance, T - the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

wavenumber, $\bar{\nu}$ - the number of waves per unit length.

Note: The usual unit of wavenumber is the reciprocal centimeter, cm^{-1}. The wavenumber is the reciprocal of the wavelength, λ, when λ is expressed in centimeters.

zero-filling - the addition of zero-valued points to the end of a measured interferogram.

Note: Performing the FT of a zero-filled interferogram results in correctly interpolated points in the computed spectrum.

A.2 Definitions of Mathematical Symbols

A, absorbance - the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A = \log_{10}\left(\frac{1}{T}\right) = -\log_{10}T$$

AAI_{im} - band area of the i^{th} analyte in the m^{th} analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i) .

AAV_{im} - average absorbance of the i^{th} analyte in the m^{th} analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i) .

ASC, accepted standard concentration - the concentration value assigned to a chemical standard.

ASCPP, accepted standard concentration-pathlength product - for a chemical standard, the product of the ASC and the sample absorption pathlength. The units "centimeters-ppm" or "meters-ppm" are recommended.

AU_i, analytical uncertainty limit - the maximum permissible fractional uncertainty of analysis for the i^{th} analyte concentration, expressed as a fraction of the analyte concentration determined in the analysis.

AVT_m - average estimated total absorbance in the m^{th} analytical region.

$CKWN_k$ - estimated concentration of the k^{th} known interferant.

$CMAX_i$ - estimated maximum concentration of the i^{th} analyte.

$CPOT_j$ - estimated concentration of the j^{th} potential interferant.

DL_i, required detection limit - for the i^{th} analyte, the lowest concentration of the analyte for which its overall fractional uncertainty (OFU_i) is required to be less than the analytical uncertainty limit (AU_i).

FC_m - center wavenumber position of the m^{th} analytical region.

FAU_i, fractional analtyical uncertainty - calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the mathematical comparison of reference and sample spectra.

FCU_i, fractional calibration uncertainty - calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in Beer's law modeling of the reference spectra concentrations.

FFL_m - lower wavenumber position of the CTS absorption band associated with the m^{th} analytical region.

FFU_m - upper wavenumber position of the CTS absorption band associated with the m^{th} analytical region.

FL_m - lower wavenumber position of the m^{th} analytical region.

FMU_i, fractional model uncertainty - calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the absorption model employed.

FN_L - lower wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

FN_U - upper wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

FRU_i, fractional reproducibility uncertainty - calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the reproducibility of spectra from the FTIR system.

FU_m - upper wavenumber position of the m^{th} analytical region.

IAI_{jm} - band area of the j^{th} potential interferant in the m^{th} analytical region, at its expected concentration ($CPOT_j$).

IAV_{im} - average absorbance of the i^{th} analyte in the m^{th} analytical region, at its expected concentration ($CPOT_j$).

$ISC_{i\ or\ k}$, indicated standard concentration - the concentration from the computerized analytical program for a single-compound reference spectrum for the i^{th} analyte or k^{th} known interferant.

kPa - kilo-Pascal (see Pascal).

L_S' - estimated sample absorption pathlength.

L_R - reference absorption pathlength.

L_S - actual sample absorption pathlength.

MAU_i - mean of the MAU_{im} over the appropriate analytical regions.

MAU_{im}, minimum analyte uncertainty - the calculated minimum concentration for which the analytical uncertainty limit (AU_i) in the measurement of the i^{th} analyte, based on spectral data in the m^{th} analytical region, can be maintained.

MIU_j - mean of the MIU_{jm} over the appropriate analytical regions.

MIU_{jm}, minimum interferant uncertainty - the calculated minimum concentration for which the analytical uncertainty limit $CPOT_j/20$ in the measurement of the j^{th} interferant, based on spectral data in the m^{th} analytical region, can be maintained.

MIL, minimum instrumental linewidth - the minimum linewidth from the FTIR system, in wavenumbers.

Note: The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the system. The MIL is fundamentally limited by the retardation of the interferometer, but is also affected by other operational parameters (e.g., the choice of apodization).

N_i - number of analytes.

N_j - number of potential interferants.

N_k - number of known interferants.

N_{scan} - the number of scans averaged to obtain an interferogram.

OFU_i - the overall fractional uncertainty in an analyte concentration determined in the analysis (OFU_i = MAX{FRU_i, FCU_i, FAU_i, FMU_i}).

Pascal (Pa) - metric unit of static pressure, equal to one Newton per square meter; one atmosphere is equal to 101,325 Pa; 1/760 atmosphere (one Torr, or one millimeter Hg) is equal to 133.322 Pa.

P_{min} - minimum pressure of the sampling system during the sampling procedure.

P_S' - estimated sample pressure.

P_R - reference pressure.

P_S - actual sample pressure.

RMS_{Sm} - measured noise level of the FTIR system in the m^{th} analytical region.

RMSD, root mean square difference - a measure of accuracy determined by the following equation:

$$RMSD = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^{n} e_i^2}$$

where:

n = the number of observations for which the accuracy is determined.

e_i = the difference between a measured value of a property and its mean value over the n observations.

Note: The RMSD value "between a set of n contiguous absorbance values (A_i) and the mean of the values" (A_M) is defined as

$$RMSD = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^{n} (A_i - A_M)^2}$$

RSA_i - the (calculated) final concentration of the i^{th} analyte.

RSI_k - the (calculated) final concentration of the k^{th} known interferant.

t_{scan}, **scan time** - time used to acquire a single scan, not including flyback.

t_S, **signal integration period** - the period of time over which an interferogram is averaged by addition and scaling of individual scans. In terms of the number of scans N_{scan} and scan time t_{scan}, $t_S = N_{scan} t_{scan}$.

t_{SR} - signal integration period used in recording reference spectra.

t_{SS} - signal integration period used in recording sample spectra.

T_R - absolute temperature of gases used in recording reference spectra.

T_S - absolute temperature of sample gas as sample spectra are recorded.

TP, Throughput - manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

V_{SS} - volume of the infrared absorption cell, including parts of attached tubing.

W_{ik} - weight used to average over analytical regions k for quantities related to the analyte i; see Appendix D.

Note that some terms are missing, e.g., BAV_m, OCU, $RMSS_m$, SUB_S, SIC_i, SAC_i, S_S

APPENDIX B

IDENTIFYING SPECTRAL INTERFERANTS

B.1 General

B.1.1 Assume a fixed absorption pathlength equal to the value L_S'.

B.1.2 Use band area calculations to compare the relative absorption strengths of the analytes and potential interferants. In the m^{th} analytical region (FL_m to FU_m), use either rectangular or trapezoidal approximations to determine the band areas described below (see Reference A, Sections A.3.1 through A.3.3); document any baseline corrections applied to the spectra.

B.1.3 Use the average total absorbance of the analytes and potential interferants in each analytical region to determine whether the analytical region is suitable for analyte concentration determinations.

> Note: The average absorbance in an analytical region is the band area divided by the width of the analytical region in wavenumbers. The average total absorbance in an analytical region is the sum of the average absorbances of all analytes and potential interferants.

B.2 Calculations

B.2.1 Prepare spectral representations of each analyte at the concentration $CL_i = (DL_i)(AU_i)$, where DL_i is the required detection limit and AU_i is the maximum permissible analytical uncertainty. For the m^{th} analytical region, calculate the band area (AAI_{im}) and average absorbance (AAV_{im}) from these scaled analyte spectra.

B.2.2 Prepare spectral representations of each potential interferant at its expected concentration ($CPOT_j$). For the m^{th} analytical region, calculate the band area (IAI_{jm}) and average absorbance (IAV_{jm}) from these scaled potential interferant spectra.

FIGURE B.1 Presentation of Potential Interferant Calculations

	Analytical Regions 1 . . . . . M
Analyte Labels	
1	AAI_{11} . . . AAI_{1M}
.	. .
.	. .
I	AAI_{I1} . . . AAI_{IM}
Potential Interferant Labels	
1	IAI_{11} . . . IAI_{1M}
.	. .
.	. .
J	IAI_{J1} . . . IAI_{JM}

FIGURE B.2 Presentation of Known Interferant Calculations

	Analytical Regions 1 . . . . M
	Analyte Labels
1	AAI_{11} . . . . AAI_{1M}
.	. .
.	. .
I	AAI_{I1} . . . . AAI_{IM}
	Known Interferant Labels
1	IAI_{11} . . . . IAI_{1M}
.	. .
.	. .
K	IAI_{K1} . . . . IAI_{KM}
Total Average Absorbance	AVT_1 AVT_M

B.2.3 Repeat the calculation for each analytical region, and record the band area results in matrix form as indicated in Figure B.1.

B.2.4 If the band area of any potential interferant in an analytical region is greater than the one-half the band area of any analyte (i.e., $IAI_{jm} > 0.5\ AAI_{im}$ for any pair ij and any m), classify the potential interferant as known interferant. Label the known interferants k = 1 to K. Record the results in matrix form as indicated in Figure B.2.

B.2.5 Calculate the average total absorbance (AVT_m) for each analytical region and record the values in the last row of the matrix described in Figure B.2. Any analytical region where $AVT_m > 2.0$ is unsuitable.

APPENDIX C

ESTIMATING NOISE LEVELS

C.1 General

C.1.1 The root-mean-square (RMS) noise level is the standard measure of noise in this Protocol. The RMS noise level of a contiguous segment of a spectrum is defined as the RMS difference (RMSD) between the absorbance values which form the segment and the mean value of that segment (see Appendix A).

C.1.2 The RMS noise value in double-beam absorbance spectra is assumed to be inversely proportional to: (a) the square root of the signal integration period of the sample single beam spectra from which it is formed, and (b) to the total infrared power transmitted through the interferometer and absorption cell.

C.1.3 Practically, the assumption of C.1.2 allow the RMS noise level of a complete system to be estimated from the following four quantities:

(a) RMS_{MAN} - the noise level of the system (in absorbance units), without the absorption cell and transfer optics, under those conditions necessary to yield the specified minimum instrumental linewidth, e.g., Jacquinot stop size.

(b) t_{MAN} - the manufacturer's signal integration time used to determine RMS_{MAN}.

(c) t_{SS} - the signal integration time for the analyses.

(d) TP - the manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

C.2 Calculations

C.2.1 Obtain the values of RMS_{MAN}, t_{MAN}, and TP from the manufacturers of the equipment, or determine the noise level by direct measurements with the completely constructed system proposed in Section 4.

C.2.2 Calculate the noise value of the system (RMS_{EST}) as follows:

$$RMS_{EST} = RMS_{MAN} \quad TP \sqrt{\frac{t_{ss}}{t_{MAN}}}$$

APPENDIX D

ESTIMATING MINIMUM CONCENTRATION MEASUREMENT UNCERTAINTIES (MAU and MIU)

D.1 General

Estimate the minimum concentration measurement uncertainties for the i^{th} analyte (MAU_i) and j^{th} interferant (MIU_j) based on the spectral data in the m^{th} analytical region by comparing the analyte band area in the analytical region (AAI_{im}) and estimating or measuring the noise level of the system (RMS_{EST} or RMS_{Sm}).

> Note: For a single analytical region, the MAU or MIU value is the concentration of the analyte or interferant for which the band area is equal to the product of the analytical region width (in wavenumbers) and the noise level of the system (in absorbance units). If data from more than one analytical region is used in the determination of an analyte concentration, the MAU or MIU is the mean of the separate MAU or MIU values calculated for each analytical region.

D.2 Calculations

D.2.1 For each analytical region, set RMS = RMS_{Sm} if measured (Appendix G), or set RMS = RMS_{EST} if estimated (Appendix C).

D.2.2 For each analyte associated with the analytical region, calculate

$$MAU_{im} = (RMS)\,(DL_i)\,(AU_i)\,\frac{(FU_m - FL_m)}{AAI_{im}}$$

D.2.3 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $MAU_i = MAU_{im}$.

D.2.4 If a number of analytical regions are used to calculate the concentration of the i^{th} analyte, set MAU_i equal to the weighted mean of the appropriate MAU_{im} values calculated above; the weight for each term in the mean is equal to the fraction of the total wavenumber range used for the calculation represented by each analytical region. Mathematically, if the set of analytical regions employed is {m'}, then the MAU for each analytical region is

$$MAU_i = \sum_{k \in \{m'\}} W_{ik}\ MAU_{ik}$$

where the weight W_{ik} is defined for each term in the sum as

$$W_{ik} = \left(FM_k - FL_k\right)\left(\sum_{p \in \{m'\}} [FM_p - FL_p]\right)^{-1}$$

D.2.5 Repeat Sections D.2.1 through D.2.4 to calculate the analogous values MIU_j for the interferants j = 1 to J. Replace the value $(AU_i)(DL_i)$ in the above equations with $CPOT_j/20$; replace the value AAI_{im} in the above equations with IAI_{jm}.

APPENDIX E

DETERMINING FRACTIONAL REPRODUCIBILITY UNCERTAINTIES (FRU)

E.1 General

To estimate the reproducibility of the spectroscopic results of the system, compare the CTS spectra recorded before and after preparing the reference spectra. Compare the difference between the spectra to their average band area. Perform the calculation for each analytical region on the portions of the CTS spectra associated with that analytical region.

E.2 Calculations

E.2.1 The CTS spectra {R1} consist of N spectra, denoted by S_{1i}, i=1, N. Similarly, the CTS spectra {R2} consist of N spectra, denoted by S_{2i}, i=1, N. Each S_{ki} is the spectrum of a single compound, where i denotes the compound and k denotes the set {Rk} of which S_{ki} is a member. Form the spectra S_3 according to $S_{3i} = S_{2i}-S_{1i}$ for each i. Form the spectra S_4 according to $S_{4i} = [S_{2i}+S_{1i}]/2$ for each i.

E.2.2 Each analytical region m is associated with a portion of the CTS spectra S_{2i} and S_{1i}, for a particular i, with lower and upper wavenumber limits FFL_m and FFU_m, respectively.

E.2.3 For each m and the associated i, calculate the band area of S_{4i} in the wavenumber range FFU_m to FFL_m. Follow the guidelines of Section B.1.2 for this band area calculation. Denote the result by BAV_m.

E.2.4 For each m and the associated i, calculate the RMSD of S_{3i} between the absorbance values and their mean in the wavenumber range FFU_m to FFL_m. Denote the result by $SRMS_m$.

E.2.5 For each analytical region m, calculate the quantity

$$FM_m = SRMS_m(FFU_m-FFL_m)/BAV_m$$

E.2.6 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $FRU_i = FM_m$.

E.2.7 If a number p_i of analytical regions are used to calculate the concentration of the i^{th} analyte, set FRU_i equal to the weighted mean of the appropriate FM_m values calculated above. Mathematically, if the set of analytical regions employed is {m'}, then

$$FRU_i = \sum_{k \in \{m'\}} W_{ik} \quad FM_k$$

where the W_{ik} are calculated as described in Appendix D.

APPENDIX F

DETERMINING FRACTIONAL CALIBRATION UNCERTAINTIES (FCU)

F.1 General

F.1.1 The concentrations yielded by the computerized analytical program applied to each single-compound reference spectrum are defined as the indicated standard concentrations (ISC's). The ISC values for a single compound spectrum should ideally equal the accepted standard concentration (ASC) for one analyte or interferant, and should ideally be zero for all other compounds. Variations from these results are caused by errors in the ASC values, variations from the Beer's law (or modified Beer's law) model used to determine the concentrations, and noise in the spectra. When the first two effects dominate, the systematic nature of the errors is often apparent; take steps to correct them.

F.1.2 When the calibration error appears non-systematic, apply the following method to estimate the fractional calibration uncertainty (FCU) for each compound. The FCU is defined as the mean fractional error between the ASC and the ISC for all reference spectra with non-zero ASC for that compound. The FCU for each compound shall be less than the required fractional uncertainty specified in Section 4.1.

F.1.3 The computerized analytical programs shall also be required to yield acceptably low concentrations for compounds with ISC=0 when applied to the reference spectra. The limits chosen in this Protocol are that the ISC of each reference spectrum for each analyte or interferant shall not exceed that compound's minimum measurement uncertainty (MAU or MIU).

F.2 Calculations

F.2.1 Apply each analytical program to each reference spectrum. Prepare a similar table as that in Figure F.1 to present the ISC and ASC values for each analyte and interferant in each reference spectrum. Maintain the order of reference file names and compounds employed in preparing Figure F.1.

F.2.2 For all reference spectra in Figure F.1, verify that the absolute value of the ISC's are less than the compound's MAU (for analytes) or MIU (for interferants).

F.2.3 For each analyte reference spectrum, calculate the quantity (ASC-ISC)/ASC. For each analyte, calculate the mean of these values (the FCU_i for the i^{th} analyte) over all reference spectra. Prepare a similar table as that in Figure F.2 to present the FCU_i and analytical uncertainty limit (AU_i) for each analyte.

FIGURE F.1
Presentation of Accepted Standard Concentrations (ASC's)
and Indicated Standard Concentrations (ISC's)

Compound Name	Reference Spectrum File Name	ASC (ppm)	ISC (ppm) Analytes i=1.....I Interferants j=1.....J					

FIGURE F.2
Presentation of Fractional Calibration Uncertainties (FCU's)
and Analytical Uncertainties (AU's)

Analyte Name	FCU (%)	AU (%)

APPENDIX G

MEASURING NOISE LEVELS

G.1 General

The root-mean-square (RMS) noise level is the standard measure of noise. The RMS noise level of a contiguous segment of a spectrum is the RMSD between the absorbance values that form the segment and the mean value of the segment (see Appendix A).

G.2 Calculations

G.2.1 Evacuate the absorption cell or fill it with UPC grade nitrogen at approximately one atmosphere total pressure.

G.2.2 Record two single beam spectra of signal integration period t_{SS}.

G.2.3 Form the double beam absorption spectrum from these two single beam spectra, and calculate the noise level RMS_{Sm} in the M analytical regions.

APPENDIX H

DETERMINING SAMPLE ABSORPTION PATHLENGTH (L_S) AND FRACTIONAL ANALYTICAL UNCERTAINTY (FAU)

H.1 General

Reference spectra recorded at absorption pathlength (L_R), gas pressure (P_R), and gas absolute temperature (T_R) may be used to determine analyte concentrations in samples whose spectra are recorded at conditions different from that of the reference spectra, i.e., at absorption pathlength (L_S), absolute temperature (T_S), and pressure (P_S). Appendix H describes the calculations for estimating the fractional uncertainty (FAU) of this practice. It also describes the calculations for determining the sample absorption pathlength from comparison of CTS spectra, and for preparing spectra for further instrumental and procedural checks.

H.1.1 Before sampling, determine the sample absorption pathlength using least squares analysis. Determine the ratio L_S/L_R by comparing the spectral sets {R1} and {R3}, which are recorded using the same CTS at L_S and L_R, and T_S and T_R, but both at P_R.

H.1.2 Determine the fractional analysis uncertainty (FAU) for each analyte by comparing a scaled CTS spectral set, recorded at L_S, T_S, and P_S, to the CTS reference spectra of the same gas, recorded at L_R, T_R, and P_R. Perform the quantitative comparison after recording the sample spectra, based on band areas of the spectra in the CTS absorbance band associated with each analyte.

H.2 Calculations

H.2.1 Absorption Pathlength Determination. Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R3}. Form a one-dimensional array $\mathbf{A}_R$ containing the absorbance values from all segments of {R1} that are associated with the analytical regions; the members of the array are A_{Ri}, i = 1, n. Form a similar one-dimensional array $\mathbf{A}_S$ from the absorbance values in the spectral set {R3}; the members of the array are A_{Si}, i = 1, n. Based on the model $\mathbf{A}_S = r\mathbf{A}_R + \mathbf{E}$, determine the least-squares estimate of r', the value of r which minimizes the square error $\mathbf{E}^2$. Calculate the sample absorption pathlength $L_S = r'(T_S/T_R)L_R$.

H.2.2 Fractional Analysis Uncertainty. Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R4}. Form the arrays $\mathbf{A}_S$ and $\mathbf{A}_R$ as described in Section H.2.1, using values from {R1} to form $\mathbf{A}_R$, and values from {R4} to form $\mathbf{A}_S$. Calculate the values

$$NRMS_E = \sqrt{\sum_{i=1}^{n} \left[A_{Si} - \left(\frac{T_R}{T_S} \right) \left(\frac{L_S}{L_R} \right) \left(\frac{P_S}{P_R} \right) A_{Ri} \right]^2}$$

and

$$IA_{AV} = \frac{1}{2} \sum_{i=1}^{n} \left[A_{Si} + \left(\frac{T_R}{T_S} \right) \left(\frac{L_S}{L_R} \right) \left(\frac{P_S}{P_R} \right) A_{Ri} \right]$$

The fractional analytical uncertainty is defined as

$$FAU = \frac{NRMS_E}{IA_{AV}}$$

APPENDIX I

DETERMINING FRACTIONAL MODEL UNCERTAINTIES (FMU)

I.1 General

To prepare analytical programs for FTIR analyses, the sample constituents must first be assumed; the calculations in this appendix, based upon a simulation of the sample spectrum, verify the appropriateness of these assumptions. The simulated spectra consist of the sum of single compound reference spectra scaled to represent their contributions to the sample absorbance spectrum; scaling factors are based on the indicated standard concentrations (ISC) and measured (sample) analyte and interferant concentrations, the sample and reference absorption pathlengths, and the sample and reference gas pressures. No band-shape correction for differences in the temperature of the sample and reference spectra gases is made; such errors are included in the FMU estimate. The actual and simulated sample spectra are quantitatively compared to determine the fractional model uncertainty; this comparison uses the reference spectra band areas and residuals in the difference spectrum formed from the actual and simulated sample spectra.

I.2 Calculations

I.2.1 For each analyte (with scaled concentration RSA_i), select a reference spectrum SA_i with indicated standard concentration ISC_i. Calculate the scaling factors

$$RA_i = \frac{T_R\, L_S\, P_S\, RSA_i}{T_S\, L_R\, P_R\, ISC_i}$$

and form the spectra SAC_i by scaling each SA_i by the factor RA_i.

I.2.2 For each interferant, select a reference spectrum SI_k with indicated standard concentration ISC_k. Calculate the scaling factors

$$RI_k = \frac{T_R\, L_S\, P_S\, RSI_k}{T_S\, L_R\, P_R\, ISC_k}$$

and form the spectra SIC_k by scaling each SI_k by the factor RI_k.

I.2.3 For each analytical region, determine by visual inspection which of the spectra SAC_i and SIC_k exhibit absorbance bands within the analytical region. Subtract each spectrum SAC_i and SIC_k exhibiting absorbance from the sample spectrum S_S to form the spectrum SUB_S. To save analysis time and to avoid the introduction of unwanted noise into the subtracted spectrum, it is recommended that the calculation be made (1) only for those spectral data points within the analytical regions, and (2) for each analytical region separately using the original spectrum S_S.

I.2.4 For each analytical region m, calculate the RMSD of SUB_S between the absorbance values and their mean in the region FFU_m to FFL_m. Denote the result by $RMSS_m$.

I.2.5 For each analyte i, calculate the quantity

$$FM_m = \frac{RMSS_m \left(FFU_m - FFL_m\right) AU_i\, DL_i}{AAI_i\, RSA_i}$$

for each analytical region associated with the analyte.

I.2.6 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $FMU_i = FM_m$.

I.2.7 If a number of analytical regions are used to calculate the concentration of the i^{th} analyte, set FM_i equal to the weighted mean of the appropriate FM_m values calculated above. Mathematically, if the set of analytical regions employed is {m'}, then

$$FMU_i = \sum_{k \in \{m\}} W_{ik} \, FM_k$$

where W_{ik} is calculated as described in Appendix D.

APPENDIX J

DETERMINING OVERALL CONCENTRATION UNCERTAINTIES (OCU)

The calculations in previous sections and appendices estimate the measurement uncertainties for various FTIR measurements. The lowest possible overall concentration uncertainty (OCU) for an analyte is its MAU value, which is an estimate of the absolute concentration uncertainty when spectral noise dominates the measurement error. However, if the product of the largest fractional concentration uncertainty (FRU, FCU, FAU, or FMU) and the measured concentration of an analyte exceeds the MAU for the analyte, then the OCU is this product. In mathematical terms, set OFU_i = MAX{FRU_i, FCU_i, FAU_i, FMU_i} and OCU_i = MAX{RSA_i*OFU_i, MAU_i}.

Blank

Appendix C: Baseline Calibration Data for the ASI/Demil FT-IR System

Calibration data was collected for two separate compounds in order to establish a baseline of instrument performance that can be referenced in future work. This data will help ensure that the instrument's performance is what is expected. The data collection procedures detailed in Section III.B. were used to collect calibration data for ethylene (C_2H_4) and ethanol (C_2H_4O). This appendix simply presents the data collected and evaluates the quality of that data.

Table C.1 shows the list of files that were collected along with the data collection conditions and parameters. All calibration sample files were saved as both single beam spectra and absorbance spectra in the C:\Midac189\Calib directory on the Dell XPS D266 computer that was supplied by MRI at the onset of the ASI/DMIL FT-IR system project.

Figure C.1 shows a typical single beam spectrum that was collected during the calibration procedures. The purpose of this figure is to establish the detector envelop that should be observed when making measurements with the ASI/DMIL FT-IR system. This single beam was collected from 0 to 8000 cm^{-1} in order to show the entire detector window. Normally, spectra are collected over a smaller spectral region that is more focussed on the regions to be used for data analysis. This practice also reduces the data storage requirements

Figure C.2 and Figure C.3 are overlays of the sample absorbance spectra collected by AeroSurvey on the ASI/DMIL FT-IR system. Figures C.4 and C.5 show the corresponding Beer's law plots that were created from the spectra in Figures C.2 and C.3. The MicrosoftR Excel '97 spreadsheet files created for these data can also be found in C:\Midac189\Calib on the Dell XPS D266.

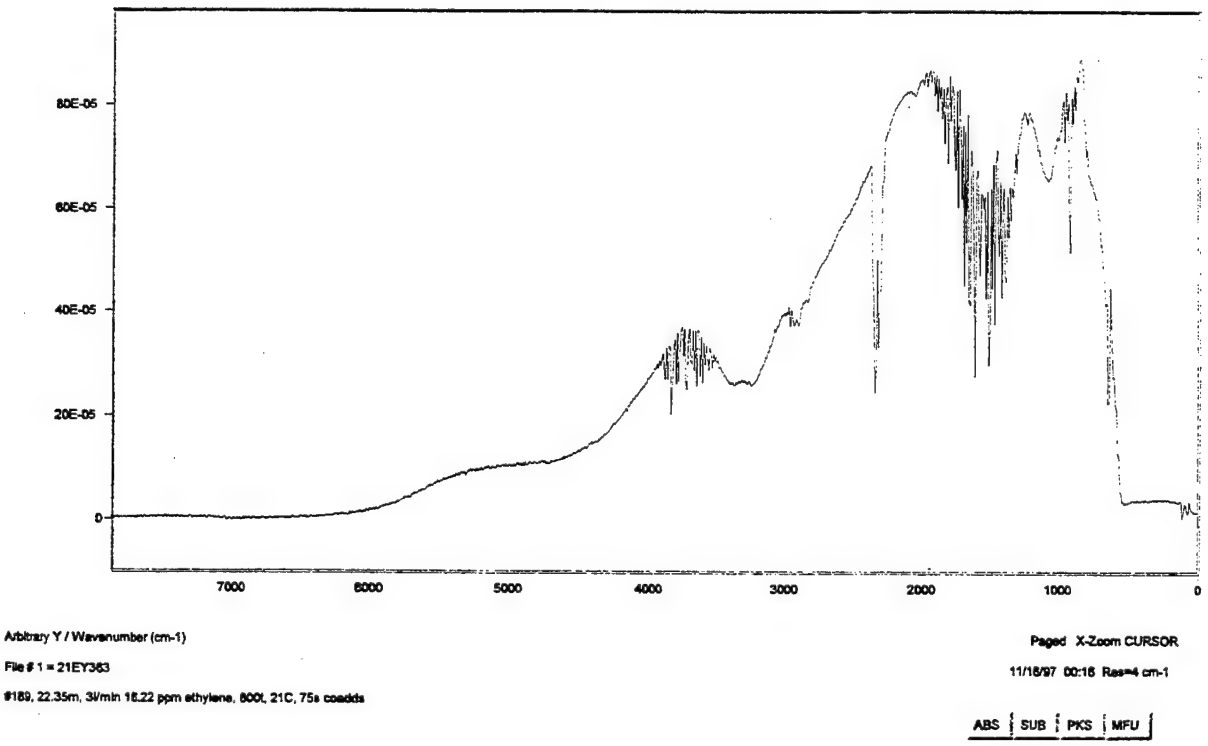


Figure C.1. An example of a typical single beam collected by AeroSurvey with the ASI/Demil FT-IR system.

Table C.1 **Calibration files collected using Midac #189 with the MRI white cell set at 22.35 m (2 rows of 20 laser dots each). Files are located in C:\Midac189\calib on the Dell XPS D266. Files named *.spc are single beam spectra and files named *.abs are absorbance spectra.**

Filename	Date	Flow Rate (l/min)	Sample P (torr)	Sample T (C)	Cell Contents
eabkg01	971115	3	800	21	N_2
21ea230	971115	3	800	21	10.28 ppm ethanol
21ea432	971115	3	800	21	19.31 ppm ethanol
21ea858	971115	3	800	21	38.37 ppm ethanol
21ea1692	971115	3	800	21	75.72 ppm ethanol
eabkg02	971115	3	800	21	N_2
eybkd01	971115	3	800	21	N_2
21ey44	971115	3	800	21	10.28 ppm ethylene
21ey91	971115	3	800	21	19.31 ppm ethylene
21ey182	971115	3	800	21	38.37 ppm ethylene
21ey363	971115	3	800	21	75.72 ppm ethanol
eybkg02	971115	3	800	21	N_2
eaprg1*	971115	3	800	21	filling cell with ethanol after N_2 purge
n2prg1*	971115	3	800	21	purging cell with N_2 after ethanol sample
n2prg2*	971115	3	800	21	purging cell with N_2 after ethanol sample
n2prg3*	971115	3	800	21	purging cell with N_2 after ethylene sample

* - Files are mulitfiles containing absorbance spectra. These files are located in C:\Midac189\calib on the Dell XPS D266.

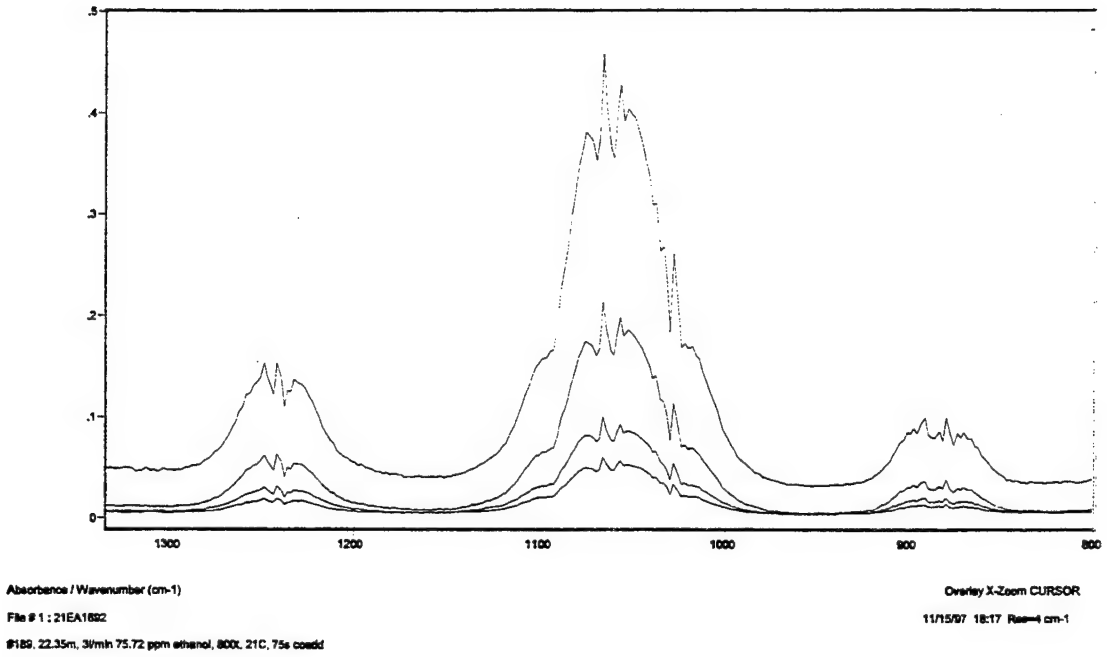


Figure C.2 An overlay of the four calibration files collected for ethanol by AeroSurvey on the ASI/Demil FT-IR system.

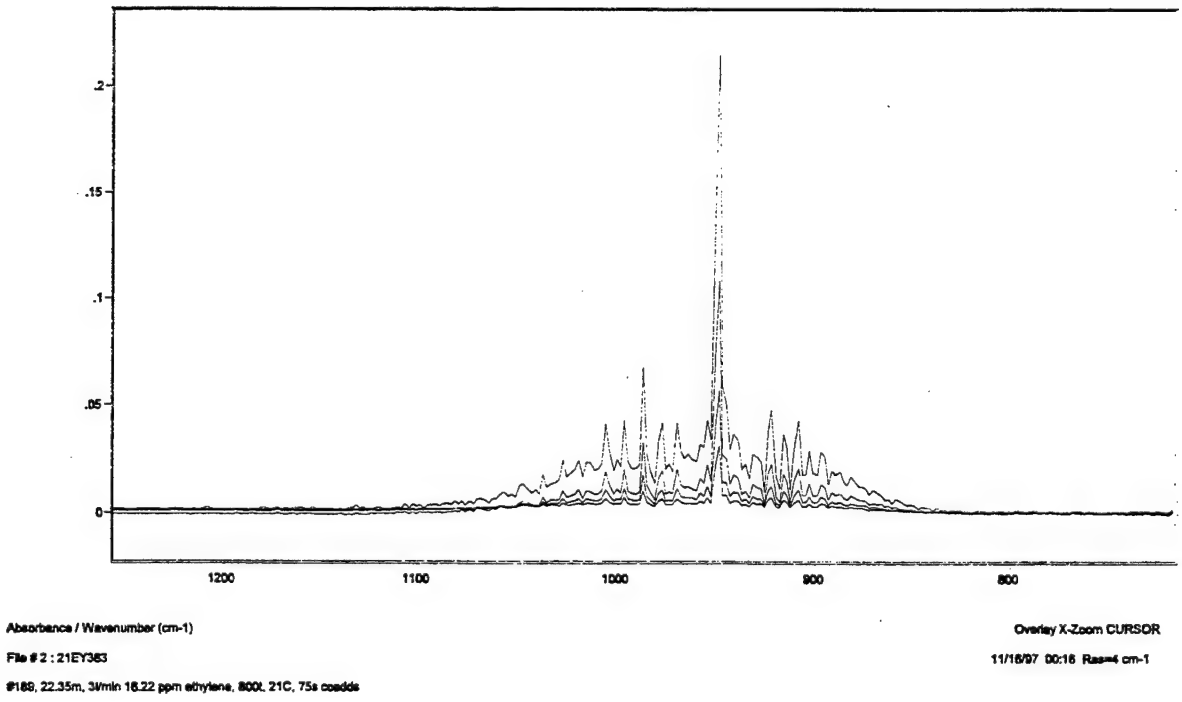


Figure C.3 An overlay of the four calibration spectra collected by AeroSurvey on the ASI/Demil FT-IR system.

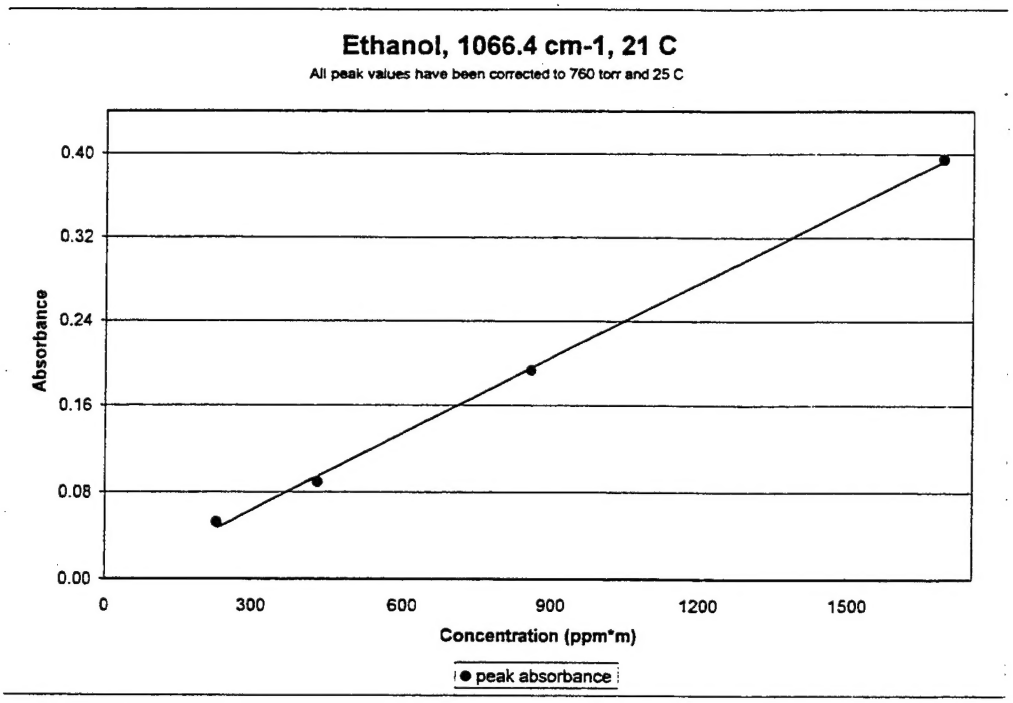


Figure C.4 Beer's law plot for ethanol.

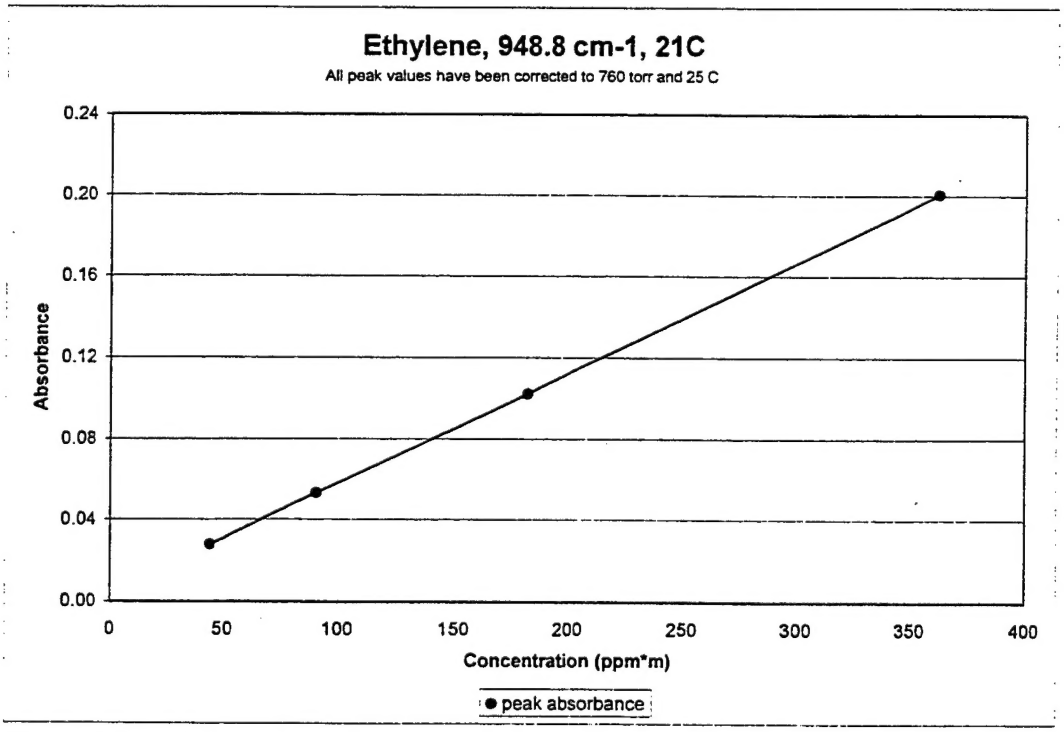


Figure C.5 The Beer's law plot for ethylene.

Appendix D: Gas Flow and Purging Characteristics of the ASI/Demil FT-IR system

An experiment was performed in order to investigate the purge time required to establish a steady-state concentration in the gas cell. This experiment essentially followed the procedures described in Section III.D and Section III.E for the collection of continuous data in MDGrams/32 and the subsequent batch analysis of that data using AutoQuant.

For this procedure, the cell was initially purged with nitrogen for 60 minutes at a flow rate of 3 liters/ minute to ensure that the cell was void of any sample. After 60 minutes, a background single beam was collected using *Background Scanning*. Then, a continuous collection was started using *Kinetic Scanning*. The spectrometer was allowed to collect 4 spectra with nitrogen still flowing through the sample system. At the beginning of the collection of the fifth sample spectrum, flow of a 75.72 ppm standard of ethanol was initiated at a rate of 3 liters/ minute. A 32 coadd scan (10 seconds) spectrum was collected every fifteen seconds until the peak absorbance value at 1066 cm-1 was seen to be essentially constant.

The resulting sample spectra were analyzed for ethanol using a batch analysis in AutoQuant. These results can be seen as a concentration versus time plot in Figure D-1. This plot indicates that the concentration of ethanol had reached a steady state after approximately 20 minutes. This suggests that approximately 7 cell volumes must be flowed through the cell in order to establish a new steady state concentration.

A second continuous collection was initiated shortly after the first was completed. The first four spectra were collected of the ethanol sample. At the beginning of the fifth spectrum's collection, the flow of nitrogen was initiated at a flow rate of 3 liters/minute. Again, spectra created from 32 coadded scans (10 second integration time) were collected every 15 seconds.

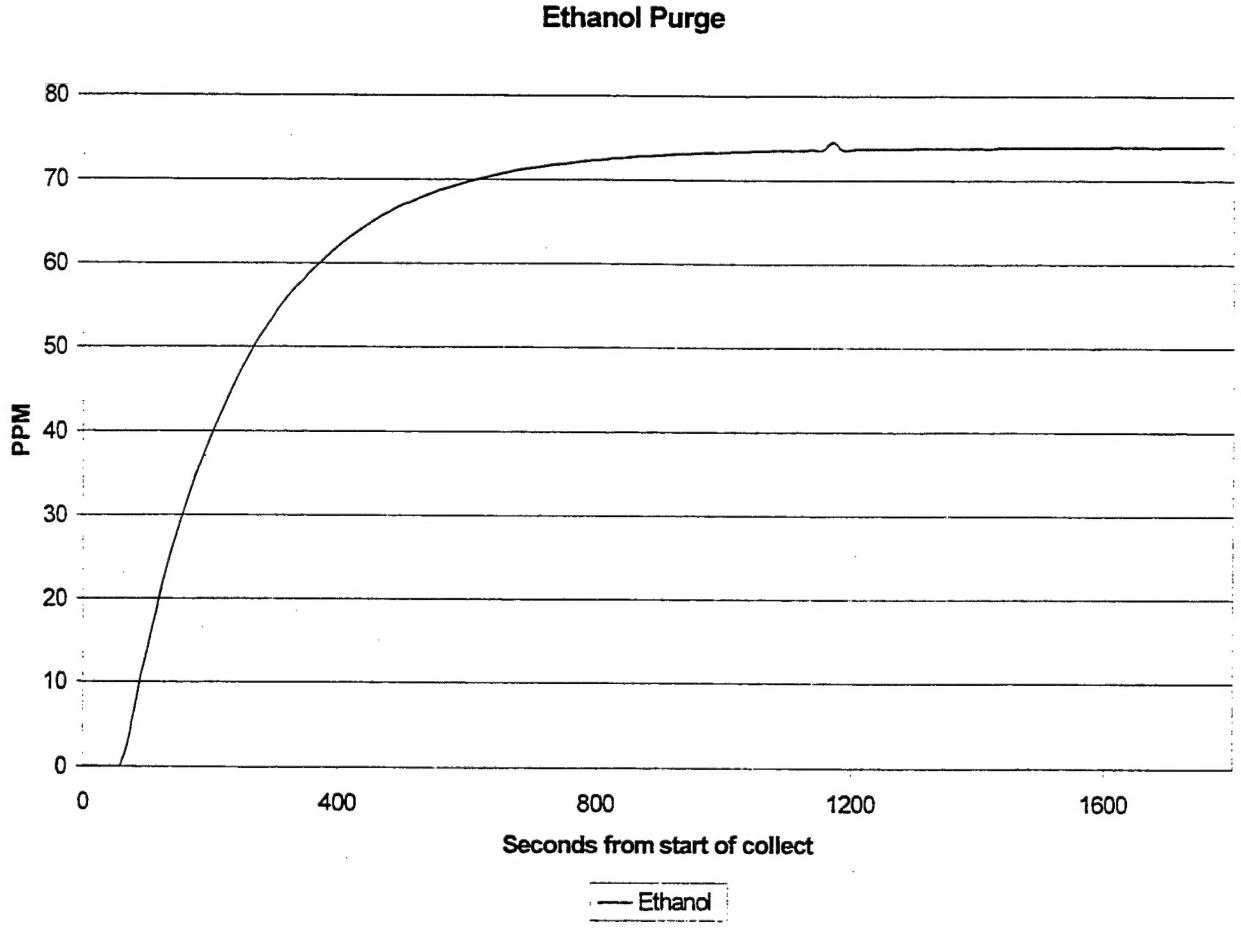


Figure D-1 Concentration vs. time as the cell was filled with a gas standard of ethanol.

The results of the second collection are shown in Figure D-2. As can be seen from Figure D-2, essentially the same amount of time (20 minutes) was required to purge the ethanol from the cell as was required to fill it earlier.

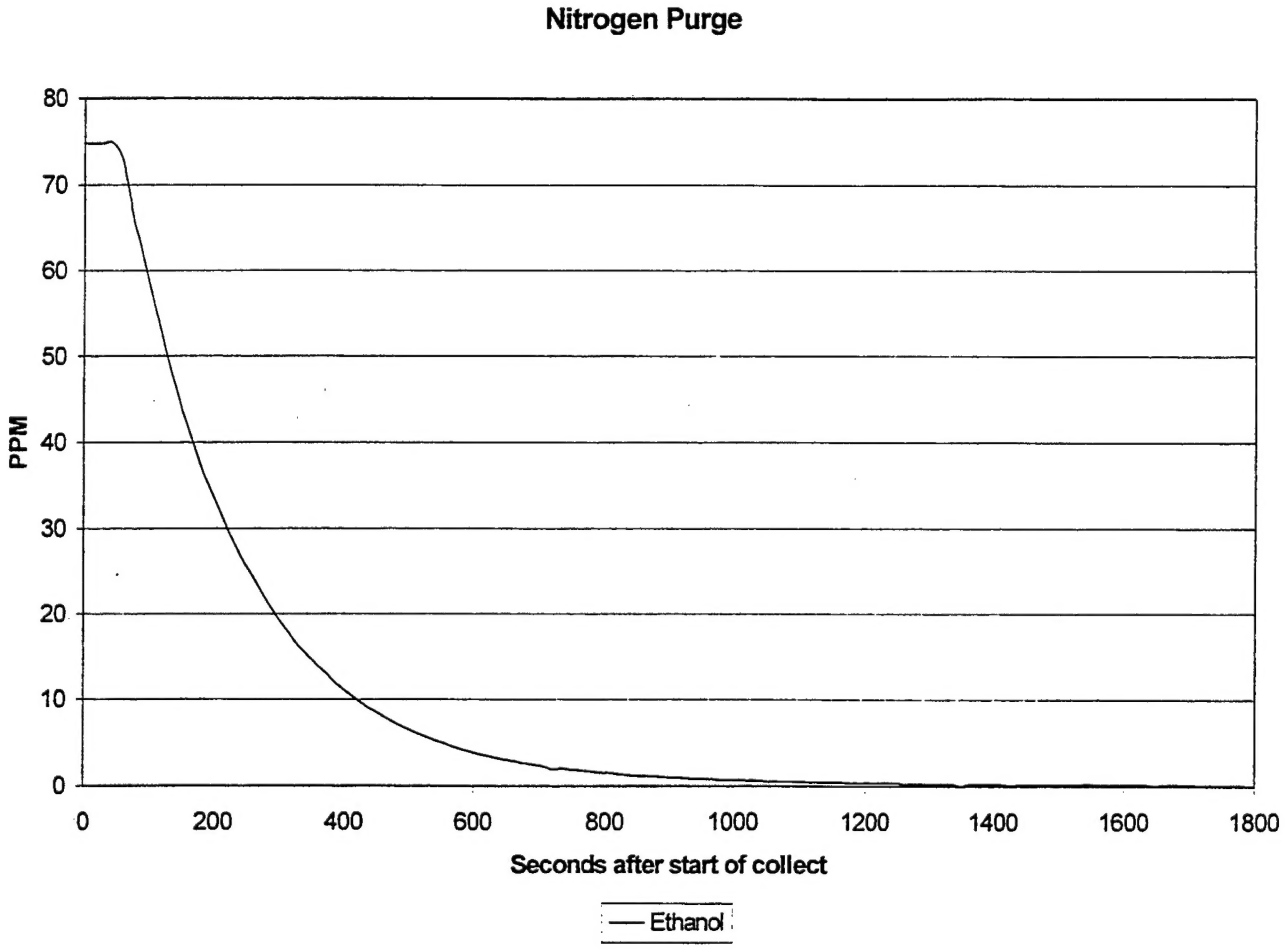


Figure D-1 Concentration vs. time as the cell was purged of ethanol with a flow of nitrogen.

Appendix E:

Midac AutoQuant™ Version 3.0: Status Update

The progress being made with Midac AutoQuant™ Version 3.0 is somewhat undetermined. The Beta Version of Midac AutoQuant™ 3.0 should be released sometime the week of November 17. However, AeroSurvey has discovered what appears to be a problem with the routine that Midac uses to perform the fast Fourier transform (FFT) on interferogram data. This problem seems to manifests itself in spectra of compounds with sharp absorbance features (such as ethylene), but not in spectra of compounds that have broad absorbance features (such as ethanol). The root of the problem is not yet known. The data that demonstrates the problem has been sent to Midac for investigation by their programmers. Until this problem is solved and Midac AutoQuant™ has been tested thoroughly, data collection using Midac AutoQuant™ has been suspended.

The problem with the FFT routine used by Midac does not prevent AeroSurvey from continuing to investigate the capabilities of Midac AutoQuant™ to perform the specific tasks that MRI has indicated they require for the end use of the spectrometer system. A summary of the MRI requirements and the Midac AutoQuant™ Version 3.0 solutions follows:

- MRI needs the ability to display a continuous concentration versus time plot for processes being monitored. Midac AutoQuant™ v3.0 allows a 4-20 milliamp signal to be sent to an analog display such as a strip recorder. It may also be possible to send this signal to a CRT type monitor. The required hardware would be an analog I/O card that contained enough channels to output the 4-20 milliamp signal to all devices that require this signal.

- MRI requires that multiple alarms be allowed for an individual compound so that different levels of action can be taken for different levels of analyte present. Midac AutoQuant™ allow four alarms to be set per compound.

- MRI requires that each alarm be able to be ported-out to control a display or valve. The alarms in Midac AutoQuant™ can be tied to TTL signals that are capable of activating or closing a switch (turning on a warning light or opening and closing a valve). The TTL signals are defined as either 0 or 5 volts and can be ported-out to a switch using a TTL I/O card. Again, the TTL card must have enough channels to handle all of the devices that require a signal of this nature.

- MRI requires that the data collected using Midac AutoQuant™ be archived and accessible for mass transfer to another computer system. Midac AutoQuant™ incorporates a feature known as "Backup on the Fly". This feature writes the collected spectral data to two computer paths as the data is collected. This data can then be accessed and transferred using a communications program such as PCAnywhere™. There is some concern that the data collection rate will be affected during this process for FT-IR systems using a fast detector, such as Midac 189. This problem can be solved by preventing access to the computer during data collection periods, and allowing data transfer only between sample collections